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Energy Bands of Vanadium Oxide.

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ABSTRACT

Energy bands of vanadium oxide have been calculated by the tight binding method. For this purpose the method of Lafon and Lin has been extended to include 3p, 3d, and 4s functions, so that three-center integrals could be included in the calculations. All matrix elements were summed to convergence, and the core functions of both vanadium and oxygen are explicitly included.

The crystal potential is constructed from a superposition of spherically averaged atomic potentials. The exchange potential used consists of the $\rho^{1/3}$ approximation of Slater, together with an adjustable factor λ.

Band structures are calculated using three different crystal potentials. The density of states is computed from a sample of 505 points in 1/48 of the Brillouin zone. The effect of including core states is examined in detail, as are the effects of varying the factor λ in the exchange potential. Using the three different band structures which have been computed, an estimate of the self-consistent potential is made.

CHAPTER I

INTRODUCTION

In any investigation of the electronic properties of the solid state, it is necessary to make some approximations in order to overcome the mathematical difficulties involved. One approach to the problem is that of energy band theory, in which one considers the energy states of a single electron in a rigid, infinite, periodic lattice. The other electrons are treated as a group of noninteracting particles in the periodic potential of the lattice. Valence and conduction electrons are assumed to be in Bloch states; that is, states extended throughout the crystal and obeying the Bloch condition that

$$\psi_K(r + R_l) = e^{iK \cdot R_l} \psi_K(r)$$

where $\psi_K(r)$ is the wave function, R_l is a direct lattice vector, and K is a vector in the reciprocal lattice (Bloch, 1928). This approach has been successful in describing the properties of a wide variety of materials.

Within the approximations imposed by energy band theory, there are several methods of calculation. One is interested in solving the one electron Schrodinger equation

$$H\psi_K = E_K\psi_K ,$$

where H is the sum of the kinetic energy operator plus whatever crystal potential is being used. The various methods of calculation attack this

problem by expanding the wave function in terms of some set of known functions, such as plane waves, spherical waves, Hartree-Fock atomic wave functions, or combinations of these.

In this paper we are concerned with the energy band structure of vanadium monoxide (VO), as determined by the tight binding method. In this scheme we expand the wave function ψ_K in terms of self-consistent atomic wave functions. The details of the tight binding method are presented in the second chapter, and we will not discuss them further here. Instead we pass on to a discussion of transition-metal oxides, with particular attention to be paid to vanadium monoxide.

The transition-metal oxides have been responsible for some of the most notable failures of the band theory technique. Perhaps the best known case is that of nickel oxide (NiO). This compound has a set of partially filled overlapping d-bands and should therefore be a metal according to band theory. In reality, it is a good insulator. The same situation occurs in the monoxides of manganese (MnO) and cobalt (CoO).

The properties of many compounds in this class can, however, be explained on the basis of energy band theory. In particular, this should be true of the oxides of vanadium (Adler, 1968). The vanadium oxides are of interest because many of them undergo sudden metal-semiconductor transitions as temperature is lowered. The change in conductivity can be as large as 10^7 within a few hundredths of a degree change in temperature.

Vanadium monoxide was chosen for consideration because it was reported to undergo a very sharp transition and because it has the simplest crystal structure. At room temperature it has the sodium chloride structure, and it is stable over a wide range of composition, from $VO_{0.87}$

to $VO_{1.20}$ (Westman and Nordmark, 1960). Stoichiometric samples show a high percentage of defects on the cation and anion lattices. It has been concluded by Ariya and Golomalzina (1962), on the basis of infrared spectra, that the VO lattice consists of alternating regions of composition V_2O_3 and pure vanadium.

The lattice parameter is a function of composition, of course, and several different ranges for it has been found by different investigators. Typical values are in the range 4.024Å - 4.123Å for the composition range quoted above (Stringer, 1964). The value 4.062 was used in this calculation.

The low temperature structure is not known. It has been suggested (Schonberg, 1954) that VO breaks down into a body-centered tetragonal phase and some other phase. It was later reported that this other phase is a body-centered cubic structure (Gurevich and Ormont, 1957) or a body-centered tetragonal phase with a c/a ratio very close to unity (Westman and Nordmark, 1960). An even later study (Geld et al., 1961) concluded that this phase did not exist.

Electrical properties of VO have been studied by Morin (1959), who found that the material was semiconducting at low temperatures. At a temperature T_o = 126°K, it abruptly became metallic, with a conductivity increase of 10^6. Austin (1962) also found a semiconductor-metal transition at T_o = 126°K with the same increase in conductivity. His sample,however, was not exactly VO but was closer to $VO_{0.9}$.

Kawano et al. (1966) studied samples of various compositions in the temperature range 100° - 250°K, and did not find a transition. He found VO to be metallic throughout the range. Kawano also measured magnetic susceptibility in the temperature ranges 1.2 - 35°K and 77°K - to

300°K. He found that $VO_{1.147}$ and $VO_{1.257}$ behaved like antiferromagnets having Neel temperatures 7.0° and 4.6°K respectively. No such behavior was found for the other samples.

A later study by Warren et al. (1967) found a discontinuity of 10^4 in electrical conductivity at a temperature near 125°K. They also obtained evidence for the presence of antiferromagnetism at low temperatures.

It is readily apparent that a good deal of work remains to be done experimentally before the low temperature phase of VO can be described theoretically. Although present evidence tends to favor the existence of the metal-insulator transition, Adler (1968) describes two other situations which also fit the observed data. The first is that VO is actually a metal at all temperatures, but at some temperature T_o it decomposes into the two phases originally suggested by Klemm & Grimm (1940); that is, a body-centered tetragonal structure of composition V_3O and a higher oxide of composition V_3O_4. The phase boundaries in this material would then lead to the high resistivity. The second possibility is that samples of VO contain regions of V_2O_3 in filamentary form, which would imply that the transition observed is actually due to the V_2O_3. This is supported by the striking resemblance between VO and V_2O_3 in both electrical and magnetic behavior. The fact that VO and V_2O_3 exhibit significantly different transition temperatures seems to discourage this view. However, if one views the VO system as being V_2O_3 with a large vanadium excess, the crystalline distortion model which Adler applied to V_2O_3 (1967) would predict a lowering of the transition temperature. This possibility can be checked by determining the crystal structure for some crystal which actually undergoes the transition.

Assuming that the metal-insulator transition in VO does exist, we still cannot propose a model with any degree of confidence until the low temperature structure is determined. There exist two possibilities which are attractive, however. A typical face-centered cubic type antiferromagnetism at low temperatures would split the sixfold-degenerate Γ_{25}' band into two threefold degenerate bands. Since VO has 3 3d electrons per cation, this could explain its low temperature behavior. This model,of course, depends upon the transition taking place at the Neel temperature. Another possibility is the crystal distortion model proposed by Adler (1967) for V_2O_3. In the case of VO Adler suggests that the distortion is a rhombohedral pairing of alternate (111) planes. Of course a third model could be a combination of the two. Since it is not certain that VO actually undergoes a metal-insulator transition, no model will be proposed in this paper.

The second chapter of this paper will be devoted to a discussion of the tight binding method and the crystal potential which was used in this calculation. The third chapter will be concerned with the details of the calculation, the fourth chapter will give the results obtained, and the fifth chapter will give the conclusions to be drawn.

CHAPTER II

In this chapter we will discuss the tight binding, or LCAO, method of calculating energy bands. The matrix elements for this method will be derived and the integrals necessary to compute them will be given. The crystal potential and exchange potential will also be discussed. Much of the following discussion is taken from Callaway (1964).

The tight binding method was proposed by Bloch in 1928. Until recently, however, use of the method has been largely restricted either to calculations of a highly empirical nature or to ones in which it serves as an interpolation scheme after energy bands have been calculated at symmetry points by other methods. The technique has been improved, however, by Lafon and Lin (1966) and this, together with the increased efficiency of modern computers, has made the tight binding approximation an effective tool for calculating energy bands.

The method is based upon the expansion of the crystalline electronic wave function in terms of bound atomic states. The atomic wave functions must be combined to form functions which have the periodicity required by Bloch's theorem. It can be easily shown that the Bloch function Φ_K given by

$$\Phi_K(\underset{\sim}{r}) = \frac{1}{\sqrt{N}} \sum_{\nu} e^{i\underset{\sim}{K}\cdot\underset{\sim}{R}_\nu} u(\underset{\sim}{r} - \underset{\sim}{R}_\nu)$$

where $u(\underset{\sim}{r} - \underset{\sim}{R}_\nu)$ is an atomic function centered at lattice site R_ν, does satisfy the Bloch condition

$$\Phi_K(\underset{\sim}{r} + \underset{\sim}{R}_l) = e^{i\underset{\sim}{K}\cdot\underset{\sim}{R}_l} \Phi_K(\underset{\sim}{r}) ,$$

where $\underset{\sim}{R}_j$ is a direct lattice vector.

The set consisting of only the bound atomic states does not form a complete set, so an expansion of the wave function using this set as a basis does not lead to an exact solution of the Schrodinger equation. However, the inclusion of all the bound states can be expected to yield a good approximation to the actual wave function.

We will now consider the matrix elements which occur in the tight binding formulation. Since atomic states on different atoms are not orthogonal, the secular determinant has the form

$$|H_{i,j}(K) - E\, S_{i,j}(K)| = 0,$$

where $H_{i,j}$ and $S_{i,j}$ are the matrix elements of the Hamiltonian and of unity with respect to the basis of Bloch functions formed from atomic functions having symmetry properties i and j, respectively. The expressions for these matrix elements will now be derived.

Writing the Hamiltonian to yield energy in Rydbergs, we have

$$H = -\nabla^2 + \sum_\nu V(\underset{\sim}{r} - \underset{\sim}{R}_\nu) + VX$$

$$= -\nabla^2 + V + VX$$

where $V(\underset{\sim}{r} - \underset{\sim}{R}_\nu)$ is the potential centered on the atom at lattice site R_ν and VX is the exchange. We will temporarily ignore the exchange term.

$$H_{i,j}(K) = \int \Phi_{K,i} H \Phi_{K,j} d^3r$$

$$= \int \frac{1}{\sqrt{N}} \sum_\nu e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_\nu} u_i^*(r - R_\nu)[-\nabla^2 + V]$$

$$\frac{1}{\sqrt{N}} \sum_{\nu''} e^{i\underset{\sim}{K}\cdot\underset{\sim}{R}_{\nu''}} u_j(\underset{\sim}{r} - \underset{\sim}{R}_{\nu''}) d^3r$$

$$= \frac{1}{N} \sum_{\nu,\nu''} e^{-i\underset{\sim}{K}\cdot(\underset{\sim}{R}_\nu - \underset{\sim}{R}_{\nu''})} \int u_i^*(\underset{\sim}{r} - \underset{\sim}{R}_\nu)[-\nabla^2 + V] u_j(\underset{\sim}{r} - \underset{\sim}{R}_{\nu''}) d^3r$$

Now the summations over ν and ν'' are both over the entire crystal, so one of them is redundant. We can simplify the expression by setting one of them (say ν'') equal to 0 and deleting the multiplier N. This yields

$$H_{i,j}(K) = \sum_\nu e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_\nu} \int u_i^*(\underset{\sim}{r} - \underset{\sim}{R}_\nu)[-\nabla^2 + V] u_j(\underset{\sim}{r}) d^3r$$

$$= \sum_\nu e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_\nu} \int u_i^*(\underset{\sim}{r} - \underset{\sim}{R}_\nu)(-\nabla^2) u_j(\underset{\sim}{r}) d^3r$$

$$+ \sum_\nu e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_\nu} \int u_i^*(\underset{\sim}{r} - \underset{\sim}{R}_\nu) V u_j(\underset{\sim}{r}) d^3r$$

$$= T_{i,j}(K) + V_{i,j}(K)$$

where

$$T_{i,j}(K) = \sum_\nu e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_\nu} \int u_i^*(\underset{\sim}{r} - \underset{\sim}{R}_\nu)(-\nabla^2) u_j(\underset{\sim}{r}) d^3r \qquad (1)$$

$$V_{i,j}(K) = \sum_\nu e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_\nu} \int u_i^*(\underset{\sim}{r} - \underset{\sim}{R}_\nu) V u_j(r) d^3r \qquad (2)$$

The matrix element of unity is given by

$$S_{i,j}(K) = \int \Phi^*_{K,i} \Phi^*_{K,j} d^3r$$

$$= \frac{1}{N} \sum_{\nu,\nu'} e^{-i\underset{\sim}{K}\cdot(\underset{\sim}{R}_\nu - \underset{\sim}{R}_{\nu'})} \int u_i^*(\underset{\sim}{r} - \underset{\sim}{R}_\nu) u_j^*(\underset{\sim}{r} - \underset{\sim}{R}_{\nu'}) d^3r$$

$$= \sum_\nu e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_\nu} \int u_i^*(\underset{\sim}{r} - \underset{\sim}{R}_\nu) u_j(r) d^3r \qquad (3)$$

The integrals in both $T_{i,j}(K)$ and $S_{i,j}(K)$ are two-center integrals; that is, they consist of one wave function centered on a site R_ν and another on the origin, with an operator which is spatially independent between them. Standard techniques of performing these integrals have been devised and are in general use, as we will discuss shortly.

The potential energy integrals in $V_{i,j}(K)$ are three-center integrals; that is, the operator between the wave functions depends upon position also. Evaluation of these integrals is therefore much more difficult. It is the problems associated with the computation of these integrals that have restricted the use of the tight binding method.

The contribution of Lin and Lafon was to devise a scheme to compute these integrals. It is based on the technique of Gaussian transformation, and will be covered in detail here.

We proceed by expanding the potential V in a Fourier series. As we will discuss shortly, V is given by a sum of atomic potentials centered on each lattice site and so has the periodicity of the lattice. Hence the Fourier expansion of V contains only reciprocal lattice vectors. We choose our origin on a vanadium atom, which gives inversion symmetry. Therefore the Fourier series contains only cosine terms. We can then write

$$V(\underset{\sim}{r}_C) = \sum_{K_\nu} V(K_\nu) \cos (\underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C)$$

where $V(K_\nu)$ is a Fourier coefficient of the potential, the summation is over all reciprocal lattice vectors, and r_C is the radius vector from any given vanadium site in the crystal.

We will now consider the integral of two 1s orbitals centered on sites A and B with the potential on site C. Using the Fourier series expansion, this becomes

$$\langle 1s(A)|V|1s(B)\rangle = \sum_{K_\nu} V(K_\nu)\ \langle 1s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C|1s(B)\rangle .$$

The wave functions used in this calculation consist of linear combinations of Slater type orbitals, so that a 1s orbital has the form $\exp(-\alpha r)$. Expressing the 1s orbitals in a Laplace transform gives

$$e^{-\alpha_1 r_A} = \frac{\alpha_1}{2\sqrt{\pi}} \int_o^\infty s_1^{-\frac{3}{2}}\ \exp\left(-\frac{\alpha_1^2}{4s_1} - r_A^2 s_1\right) ds_1$$

and similarly for the orbital on site B. This result, as well as results for several other integrals to be used in this derivation, is to be found in Tables of Integral Transforms, edited by Erdeli (1954). Putting in these expressions gives

$$\langle 1s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C|1s(B)\rangle = \frac{\alpha_1\alpha_2}{4\pi} \int_o^\infty (s_1 s_2)^{-\frac{3}{2}} \exp\left(-\frac{\alpha_1^2}{4s_1} - \frac{\alpha_2^2}{4s_2}\right)$$

$$\int \exp(-s_1 r_A^2 - s_2 r_B^2) \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C d\tau ds_1 ds_2 \qquad (4)$$

The product of two Gaussians centered on sites A and B can be written in terms of a third Gaussian centered at a point D along the line AB; that is,

$$\exp(-s_1 r_A^2 - s_2 r_B^2) = \exp\left(-\frac{s_1 s_2 r_{AB}^2}{s_1 + s_2}\right) \exp(-(s_1+s_2) r_D^2)$$

where

$$D_i = \frac{s_1 A_i + s_2 B_i}{s_1 + s_2} \quad , \quad i = x,y,z \ .$$

By writing the vector r_C as

$$r_C = r_D + r_{CD}$$

and expanding the cosine as

$$\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C = \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_D \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} - \sin \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_D \sin \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD}$$

the spatial integral in equation (4) can be evaluated.

$$\int \exp(-s_1 r_A^2 - s_2 r_B^2) \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C \, d\tau =$$

$$\exp\left(-\frac{s_1 s_2 r_{AB}^2}{s_1 + s_2}\right) \left[\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} \int \exp[-(s_1+s_2) r_D^2] \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_D \, d\tau \right.$$

$$\left. - \sin \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} \int \exp[-(s_1+s_2) r_D^2] \sin \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_D \, d\tau \right] \qquad (5)$$

The last integral in equation (5) is the integral of an odd function throughout all space, and so it vanishes. Then equation (5) becomes

$$\int \exp\left(-s_1 r_A^2 - s_2 r_B^2\right) \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C \, d\tau =$$

$$\exp\left(-\frac{s_1 s_2 r_{AB}^2}{s_1+s_2}\right) \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} 2\pi \int_0^\infty \int_0^\infty \exp[-(s_1+s_2) r_D^2]$$

$$\cos(K_\nu r_D \cos\theta) \, r_D^2 \sin\theta \, d\theta \, dr_D$$

$$= \exp\left(-\frac{s_1 s_2 r_{AB}^2}{s_1+s_2}\right) \cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r}_{CD} \frac{4\pi}{K_\nu} \int_0^\infty r_D \exp\left[-(s_1+s_2)r_D^2\right]$$

$$\sin K_\nu r_D \, dr_D$$

$$= \exp\left(-\frac{s_1 s_2 r_{AB}^2}{s_1+s_2}\right) \cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r}_{CD} \left(\frac{\pi}{s_1+s_2}\right)^{\frac{3}{2}} \exp\left(-\frac{K_\nu^2}{4(s_1+s_2)}\right) \qquad (6)$$

Now we make the following change of variable;

$$Z = s_1+s_2$$

$$u = s_1 / (s_1+s_2)$$

$$f = u(1-u)r_{AB}^2$$

$$g = K_\nu^2 + \alpha_2^2/(1-u) + \alpha_1^2/u$$

The Jacobian of this transformation is given by

$$\frac{d(s_1,s_2)}{d(u,Z)} = \begin{vmatrix} \frac{ds_2}{du} & \frac{ds_1}{dZ} \\ \frac{ds_1}{du} & \frac{ds_2}{dZ} \end{vmatrix}$$

$$= Z$$

Using this fact together with the evaluation of the spatial integral which we completed in equation (6), and noting that

$$1-u = \frac{s_2}{s_1+s_2} \ ,$$

it is a simple matter to reduce the original three-center integral to

$$\langle 1s(A)|\cos K_\nu \cdot r_C|1s(B)\rangle =$$

$$\frac{1}{4}\pi^{1/2}\alpha_1\alpha_2\int_0^1[u(1-u)]^{-3/2}\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD}du \int_0^\infty Z^{-7/2}\exp\left(-fZ - \frac{g}{4Z}\right) dZ =$$

$$2\pi\alpha_1\alpha_2 r_{AB}^3 \int_0^1 F\left[\frac{3}{(Fg)^{5/2}} + \frac{3}{(Fg)^2} + \frac{1}{(Fg)^{3/2}}\right]\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} e^{-(Fg)^{1/2}} du$$

Now we have reduced a three dimensional integral over all space to a one dimensional integral over the interval zero to one, simply by expanding the potential in a Fourier series and by using the technique of Gaussian transformation. The integral may now be easily evaluated by numerical methods. The only price we must pay for this reduction is that we have to sum the Fourier series to convergence, calculating a new integral for each value of K_ν. This is quite feasible, as will be discussed later.

Potential integrals involving higher Slater orbitals than 1s can be obtained from this integral by performing the proper partial differentiations with respect to α_1, α_2, A_x, A_y, A_z, B_x, B_y, B_z. For example,

$$\langle 2P_x(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C|1s(B)\rangle =$$

$$\int x_A e^{-\alpha_1 r_A} \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C e^{-\alpha_2 r_B} d\tau =$$

$$-\frac{d}{d\alpha_1}\left(\frac{1}{\alpha_1}\frac{d}{dA_x}\langle 1s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C|1s(B)\rangle\right).$$

For a more detailed treatment of this procedure and a tabulation of the integrals involved, see Appendix A.

Integrals computed in this fashion are compiled as previously indicated in equation (2) to form the matrix element $V_{i,j}(K)$.

The overlap integrals appear as the first term of the sum over the reciprocal lattice vectors and are compiled according to equation (3) to form the matrix element $S_{i,j}(K)$. The kinetic energy integrals could be obtained by applying the operator

$$T = -\nabla^2$$

$$= -\left(\frac{d^2}{dB_x^2} \quad \frac{d^2}{dB_y^2} \quad \frac{d^2}{dB_z^2}\right)$$

to the corresponding overlap integrals. However, methods of computing these integrals have been developed along the lines begun by Roothaan (1951). For this calculation a computer program written by Roney et al. (1968) was used for this purpose. The kinetic energy integrals were then combined according to equation (1) to form the matrix element $T_{i,j}(K)$.

This concludes our discussion of the tight binding method. We now pass on to a discussion of the crystal potential.

It is appropriate at this point to discuss the structure of vanadium oxide. VO has the sodium chloride structure; that is, it is face-centered cubic with a basis of two atoms per unit cell. The primitive translation vectors of the direct lattice are

$$\underset{\sim}{a}_1 = \frac{a}{2}(\underset{\sim}{i} + \underset{\sim}{j})$$

$$\underset{\sim}{a}_2 = \frac{a}{2}(\underset{\sim}{j} + \underset{\sim}{K})$$

$$\underset{\sim}{a}_3 = \frac{a}{2}(\underset{\sim}{K} + \underset{\sim}{i})$$

where a is the lattice constant.

The reciprocal lattice vectors are given by

$$\underset{\sim}{b}_1 = \frac{2\pi}{a}(\underset{\sim}{i} + \underset{\sim}{j} - \underset{\sim}{K})$$

$$\underset{\sim}{b}_2 = \frac{2\pi}{a}(-\underset{\sim}{i} + \underset{\sim}{j} + \underset{\sim}{K})$$

$$\underset{\sim}{b}_3 = \frac{2\pi}{a}(\underset{\sim}{i} - \underset{\sim}{j} + \underset{\sim}{K})$$

For this calculation the origin was chosen at a vanadium site. The oxygen atom in the unit cell is located at

$$\underset{\sim}{R}_s = \frac{1}{2}(\underset{\sim}{a}_1 + \underset{\sim}{a}_2 + \underset{\sim}{a}_3)$$

For a general reciprocal lattice vector given by

$$\underset{\sim}{K}_n = n_1\underset{\sim}{b}_1 + n_2\underset{\sim}{b}_2 + n_3\underset{\sim}{b}_3$$

we have

$$\underset{\sim}{R}_s \cdot \underset{\sim}{K}_n = \pi(n_1 + n_2 + n_3)$$

With this background, we will consider the crystal potential.

The crystal potential was formed from a superposition of spherically averaged atomic potentials. That is,

$$V(\underset{\sim}{r}) = \sum_l V_v(\underset{\sim}{r} - \underset{\sim}{R}_l) + \sum_m V_o(\underset{\sim}{r} - \underset{\sim}{R}_m)$$

where $V_v(\underset{\sim}{r} - \underset{\sim}{R}_l)$ is an atomic potential centered on a vanadium atom at

site R_l and $V_o(\underset{\sim}{r} - \underset{\sim}{R}_m)$ is an atomic potential centered on the oxygen atom at site R_m. For reasons already discussed, we are interested in expanding this potential in a Fourier series. The Fourier coefficients are given by

$$V(K) = \frac{1}{N\Omega_o}\int V(\underset{\sim}{r})e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}}\, d^3r$$

$$= \frac{1}{N\Omega_o}\left[\sum_l \int e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}}\, V_v(\underset{\sim}{r}-\underset{\sim}{R}_l)d^3r + \sum_m \int e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}} V_o(\underset{\sim}{r}-\underset{\sim}{R}_m)d^3r\right]$$

where Ω_o is the unit cell volume and N is the number of unit cells.

Now make a change of variable from r to $r + R_l$ in the first integral and from r to $r + R_m$ in the second.

$$V(K) = \frac{1}{N\Omega_o}\left[\sum_l \int e^{-i\underset{\sim}{K}\cdot(\underset{\sim}{r}+\underset{\sim}{R}_l)} V_v(r)d^3r + \sum_m \int e^{-i\underset{\sim}{K}\cdot(\underset{\sim}{r}+\underset{\sim}{R}_m)} V_o(r)d^3r\right]$$

$$= \frac{1}{N\Omega_o}\left[\sum_l e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_l}\int V_v(\underset{\sim}{r})e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}}d^3r + \sum_m e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_m}\int V_o(r)e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}}d^3r\right]$$

By our choice of origin in the unit cell, we have

$$R_m = R_l - R_s$$

Then

$$V(K) = \frac{1}{N\Omega_o}\left[\sum_l e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_l}\int V_v(r)e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}}d^3r + \sum_l e^{-i\underset{\sim}{K}\cdot(\underset{\sim}{R}_l-\underset{\sim}{R}_s)}\int V_o(\underset{\sim}{r})e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}}d^3r\right]$$

$$= \frac{1}{N\Omega_o}\sum_l e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_l}\left[\int V_v(r)e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}}d^3r + e^{i\underset{\sim}{K}\cdot\underset{\sim}{R}_s}\int V_o(\underset{\sim}{r})e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}}d^3r\right]$$

Now

$$\sum_{1} e^{-i\underset{\sim}{K}\cdot\underset{\sim}{R}_1} = N\delta_{\underset{\sim}{K},\underset{\sim}{K}n}$$

where $\underset{\sim}{K}_n$ is a reciprocal lattice vector. As already pointed out,

$$\underset{\sim}{K}_n\cdot\underset{\sim}{R}_s = \pi(n_1 + n_2 + n_3)$$

Then

$$V(K) = \frac{1}{\Omega_o}\left[\int V_v(\underset{\sim}{r})e^{-i\underset{\sim}{K}n\cdot\underset{\sim}{r}}d^3r + e^{-i\underset{\sim}{K}n\cdot\underset{\sim}{R}s}\int V_o(r)e^{-i\underset{\sim}{K}n\cdot\underset{\sim}{r}}d^3r\right]$$

$$= \frac{1}{\Omega_o}\left[\int V_v(\underset{\sim}{r})e^{-i\underset{\sim}{K}n\cdot\underset{\sim}{r}}d^3r + (-1)^{n_1+n_2+n_3}\int V_o(r)e^{-i\underset{\sim}{K}n\cdot\underset{\sim}{r}}d^3r\right]$$

Each of the atomic potentials has the form

$$V(\underset{\sim}{r}_2) = -\frac{2Z}{\underset{\sim}{r}_2} + 2\int\frac{\rho(\underset{\sim}{r}_1)}{r_{12}}d^3r_1$$

where Z is the atomic number and ρ is the charge density. The factor of 2 converts the energy into Rydbergs. The charge density is given by

$$\rho(\underset{\sim}{r}) = \sum_{1} a_1|\psi_1|^2$$

$$= 2|\psi_{1s}|^2+2|\psi_{2s}|^2+6|\psi_{2p}|^2+2|\psi_{3s}|^2+6|\psi_{3p}|^2+3|\psi_{3d}|^2+2|\psi_{4s}|^2$$

for vanadium in the $3d^3 4s^2$ configuration. The a_1's are the occupation numbers of the 1-th states. For vanadium,

$$V(\underset{\sim}{r}_2) = -\frac{46}{\underset{\sim}{r}_2} + 2\int \frac{\rho(\underset{\sim}{r}_1)}{(r_{12})}\, d^3r_1$$

The Fourier coefficient of the vanadium potential is

$$V_v(K) = \int V_v(\underset{\sim}{r}_2) e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}_2}\, d^3r_2$$

$$= -46\int \frac{e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}_2}}{\underset{\sim}{r}_2}\, d^3r_2 + 2\iint \frac{\rho(\underset{\sim}{r}_1)}{|r_{12}|}\, e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}_2}\, d^3r_1 d^3r_2$$

Use the identity

$$\int \frac{e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}_2}}{|r_{12}|}\, d^2r_2 = \frac{4\pi}{K^2}\, e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}_1} \quad .$$

Then

$$V_v(K) = -\frac{184\pi}{K^2} + \frac{8\pi}{K^2}\int \rho(\underset{\sim}{r}_1) e^{-i\underset{\sim}{K}\cdot\underset{\sim}{r}_1}$$

$$= -\frac{184\pi}{K^2} + \frac{32\pi^2}{K^3}\int_0^\infty \rho(r_1) r_1 \sin(Kr_1)\, dr_1$$

Now take a spherical average of the charge density.

$$\rho(r_1) = \frac{1}{4\pi} \sum_1 a_1 |u_1|^2$$

where u_1 is the radial part of the wave function for the 1 - th state. Define

$$f_v(r_1) = 2|u_{1s}|^2 + 2|u_{2s}|^2 + 6|u_{2p}|^2 + 2|u_{3s}|^2 + 6|u_{3p}|^2$$

$$+ 3|u_{3d}|^2 + 2|u_{4s}|^2$$

Then

$$V_v(K) = -\frac{184\pi}{K^2} + \frac{8\pi}{K^3}\int_0^\infty r_1\, f_v(r_1)\, \sin(Kr_1)dr_1$$

Similarly

$$V_o(K) = -\frac{64\pi}{K^2} + \frac{8\pi}{K^3}\int_0^\infty r_1\, f_o(r_1)\, \sin(Kr_1)dr_1$$

where

$$f_o(r_1) = 2|u_{1s}|^2+2|u_{2s}|^2+4|u_{2p}|^2$$

From these expressions it is not at all obvious that $\lim_{K\to 0} V(K)$ exists. To show this, we will consider this term separately. Expand the sine term in a power series.

$$V_v(0) = \lim_{K\to 0} V_v(K)$$

$$= \lim_{K\to 0}\left[-\frac{184}{K^2} + \frac{8\pi}{K^3}\int f_v(r_1)\left[Kr_1 - \frac{(Kr_1)^3}{3!} + \cdots\right] r_1 dr_1\right]$$

$$= -\frac{184\pi}{K^2} + \frac{8\pi}{K^3}\int_0^\infty K\, f_v(r_1) r_1^{\,2} dr_1 - \frac{8\pi}{6K^3}K^3\int_0^\infty f_v(r_1) r_1^{\,4} dr_1$$

$$= -\frac{184\pi}{K^2} + \frac{184\pi}{K^2} - \frac{4\pi}{3}\int_0^\infty f_v(r_1) r_1^{\,4} dr_1$$

$$= -\frac{4\pi}{3}\int_0^\infty f_v(r_1) r_1^{\,4} dr_1$$

A similar expression holds, of course, for oxygen.

The radial parts of the wave functions consist of Slater-type orbitals, as tabulated by Clementi (1965). The various integrals involved in the potential can therefore be evaluated in closed form with the aid of Laplace transforms from Erdelyi (1954).

The exchange potential used consisted of the $\rho^{1/3}$ approximation of Slater, together with a multiplicative factor of λ to be adjusted. The charge density for the crystal was found at selected points within spheres centered about vanadium and oxygen atoms and having radii equal to half the nearest neighbor distance. These points were chosen so that a 96 point Gaussian formula for integration could be employed. The charge density was found by summing contributions from atomic charge densities out through nine sets of neighbors.

The cube root of the total charge density was computed along three independent axes and the results were averaged to find the final exchange result. Fourier coefficients of the exchange were calculated within the spheres centered on the vanadium and oxygen atoms and these were combined in the same manner as with the crystal potential to form the full exchange coefficient. Therefore the full Hamiltonian matrix element is given by

$$H_{i,j}(K) = V_{i,j}(K) + T_{i,j}(K) + \lambda\, VX_{i,j}(K)$$

where $VX_{i,j}(K)$ is the exchange matrix element.

Chapter III

In this chapter we will be concerned with the details of the calculation. The use of group theory will be discussed first. Then we will consider the problems involved in the computation of the three-center integrals, such as the convergence of the various sums.

The group theory for the cubic lattice has been worked out in detail (Slater, 1965) and will not be discussed at length in this chapter. A few points of particular interest for this calculation will be found in Appendix B. Here we will be more concerned with the application of group theory than with the mathematical details.

It is useful to expand the crystal wave function in terms of functions which transform according to the rows of the irreducible representations of the cubic group. This is due to the fact that the matrix elements between functions which belong to different irreducible representations, or to different rows of the same irreducible representation, are zero. Mathematically speaking,

$$H_{s,t}^{p,q} = \int f_s^{p*} H f_t^q \, d^3r$$

$$= \frac{1}{dq} \sum_{s,t} H_{s,t}^{p,q} d_{p,q} d_{s,t}$$

$$H_{s,s}^{p,p} = \frac{1}{dq} \sum_t H_{t,t}^{q,q}$$

where f_s^p is a function transforming as the s - th row of the p - th irreducible representation and similarly for f_t^q . Also dq is the dimension of the q - th irreducible representation, and the sum is over

all rows of the q - th irreducible representation.

Therefore in energy band calculations it is frequently necessary to form linear combinations of the basis functions which will transform in the proper manner. In our case the basis consisted of atomic orbitals, which already have the correct symmetry properties for a cubic lattice, so this was unnecessary. It was still necessary to combine them into Bloch sums to insure that they have the proper periodicity, as was discussed in Chapter II in connection with the tight binding method.

The matrix elements of the Hamiltonian have been given as

$$H_{i,j}(K) = \sum_l e^{-iK\cdot R_l} \int u_i^*(r-R_l)[-\nabla^2 + V + \lambda VX]\, u_j(r) d^3r$$

$$= \sum_l e^{-iK\cdot R_l} \int u_i^*(r-R_l)\, H\, u_j(r) d^3(r)$$

$$= \sum_l e^{-iK\cdot R_l} E_{i,j}(R_l)$$

where $u_i(r-R_l)$ and $u_j(r)$ are atomic orbitals centered at R_l and the origin, respectively, V is the crystal potential, λ is an adjustable parameter, and VX is the exchange.

As it stands, the sum is over all direct lattice vectors, so that we must consider separately the contribution from each atom in the crystal. The number of terms in this series can be greatly reduced by the use of group theory, however. Let R be any operation of the cubic group. Then the following is true;

$$R^{-1} = R^{\dagger} = R^*$$

$$R^{-1} H R = H$$

where H is the Hamiltonian. The quantity $E_{i,j}(R_l)$ is given by

$$E_{i,j}(R_l) = \int u_i^*(r-R_l)\, H\, u_j(r) d^3r$$

$$= \int u_i^*(r-R_l) R^{-1} H R\, u_j(r) d^3r$$

$$= \int [R\, u_i(r-R_l)]^* H\, [R\, u_j(r)]\, d^3r$$

As an example let

$$E_{i,j}(R_l) = E_{x^2-y^2, x^2-y^2}(abc) \quad ,$$

where (abc) is a general point of the direct lattice, and let R be the operator R_{19} as defined in Appendix B. Then from the transformation properties of the function $x^2 - y^2$, as given also in Appendix B, we have

$$E_{x^2-y^2, x^2-y^2}(abc) = \int [R_{19}\, u_{x^2-y^2}(r-abc)]^* H\, [R_{19}\, u_{x^2-y^2}(r)]\, d^3r$$

$$= \frac{3}{4} E_{3z^2-r^2, 3z^2-r^2}(acb) - \frac{3^{\frac{1}{2}}}{4} E_{3z^2-r^2, x^2-y^2}(acb)$$

$$+ \frac{1}{4} E_{x^2-y^2, x^2-y^2}(acb)$$

where we have related an integral between d functions transforming like $x^2 - y^2$ at a point (abc) to a group of integrals at a point (acb). By relations of this type we can express all integrals arising from a given set of neighbors in terms of the integrals arising from any one member of that set. This means that the sum over direct lattice vectors can be restricted to include only one vector from each set of neighbors, which

reduces the sum by a factor of 48 for a general set of neighbors.

For special sets of neighbors, by which is meant a set of neighbors containing less than 48 members, there exist some operations in the group which transform a vector of that set into itself. That means that not all the integrals at that point are independent; i.e., there exist relations of the type above for integrals on the same point. For maximum efficiency we could discard all but one member of each set of dependent integrals. This would substantially reduce the number of parameters involved. For example, in summing contributions from the first four sets of neighbors for functions of d symmetry, only 27 integrals need be included, out of a total of 62.

For overlap integrals the number is even fewer, since they have the symmetry properties of two-center integrals as expressed by Slater and Koster (1954). It is convenient to choose the overlap integrals in the same manner as that used for the three-center integrals, bowever. This allows the use of the same set of matrix elements to construct both energy and overlap matrices.

Use of group theory to obtain relations between integrals was of the utmost importance when programs to compute the three-center integrals were being tested. At that time all integrals were calculated, and the relations were used to detect errors in programming.

The band structure diagrams such as Figure 1 were drawn using group theory. These curves were plotted by connecting energy values whose eigenvectors transformed according to the same irreducible representation, subject to the condition that curves representing the same representations do not cross. Therefore it was necessary to know the basis functions for the various irreducible representations. Some of

these were obtained from Callaway (1964), and the remainder were computed using the character tables given by Slater (1965). At points where the symmetry changes, such as X or W, the bands were drawn with the assistance of compatibility relations found in both of the above references.

The calculation included as basis functions the wave functions for the 1s, 2s, 3s, 4s, 2p, 3p, 3d states of vanadium and the 1s, 2s, 2p states of oxygen. The eigenvalue problem therefore required the diagonalization of a 20 by 20 matrix. At symmetry points the order of the matrix could have been reduced using the orthogonality property of functions transforming according to different irreducible representations. At the point Γ, for example, we had the two dimensional representation Γ_{12}, the three dimensional representation Γ'_{25}, the one dimensional representation Γ_1 which occurred six times, and the three dimensional representation Γ_{15} which occurred three times. Therefore the matrix could have been block diagonalized into the direct sum of a two by two, three by three, six by six, and nine by nine matrix. Even these would have been further reducible, since functions transforming according to different rows of the same irreducible representation are also orthogonal. Similar results hold for other symmetry points.

However, a 20 X 20 matrix is not difficult to diagonalize, so this procedure was unnecessary. Herein lies one of the great advantages of the tight binding method over other methods. Once the necessary integrals have been computed, it is as easy to find the energies at a general point in the Brillouin zone as at a symmetry point. In other methods, such as the orthogonalized plane wave (O P W) or augmented plane wave (A P W), the secular determinant may become so large that

solutions are possible only at symmetry points where block diagonalization is possible.

We now turn our attention to the problem of computing the three-center integrals, which formed the major part of the task. Since the crystal potential was constructed from a superposition of atomic potentials, the site at which it was centered was arbitrary provided it had the same symmetry as the origin, a vanadium site. Therefore C, the lattice site of the potential, was taken to be the origin. The site B was also taken as the origin, and the direct lattice sum was performing using the point A, where A, B, and C are defined as in equation (4) of Chapter II.

Expanding the potential in a Fourier series made it necessary to sum the series to convergence in the reciprocal lattice, which was done before performing the direct lattice sum. This meant summing over every reciprocal lattice vector at each magnitude of $\underset{\sim}{K}_n$. The angular dependence of the sum was carried in the factors $\cos(\underset{\sim}{K}_n \cdot \underset{\sim}{A})$, $\sin(\underset{\sim}{K}_n \cdot \underset{\sim}{A})$, and multiples of K_x,K_y, and K_z times these, where K_x, K_y, and K_z are the components of $\underset{\sim}{K}_n$. It was possible to eliminate all terms in the sum arising from vectors having one or more negative components, by the method to be described now. Expand the cosine term as

$$\cos(\underset{\sim}{K}_n \cdot \underset{\sim}{A}) = \cos K_xA_x \cos K_yA_y \cos K_zA_z - \sin K_xA_x \sin K_yA_y \cos K_zA_z - \sin K_xA_x \cos K_yA_y \sin K_zA_z - \cos K_xA_x \sin K_yA_y \sin K_zA_z.$$

Hold the magnitudes of K_x, K_y, and K_z fixed and sum over their positive

and negative values. There are eight terms in this series, assuming that all three components are non-zero. The result is

$$\Sigma \cos(K_xA_x+K_yA_y+K_zA_z) = 8 \cos K_xA_x \cos K_yA_y \cos K_zA_z$$

where the sum is done as described. Similar results hold for $K_x \sin(\underset{\sim}{K}_n \cdot \underset{\sim}{A})$ and for terms such as $K_xK_y \cos(\underset{\sim}{K}_n \cdot \underset{\sim}{A})$, $K_x^2K_y \sin(\underset{\sim}{K}_n \cdot \underset{\sim}{A})$, $K_xK_yK_z \sin(\underset{\sim}{K}_n \cdot \underset{\sim}{A})$, etc. If one of the components K_x, K_y, K_z is 0, the factor 8 becomes 4. If two of them are 0 it becomes 2, and for the origin it is 1. These results allowed us to sum only over reciprocal lattice vectors having all components non-negative, which greatly reduced the sum.

For the special case of integrals where both functions had s symmetry, the sum was simplified even more. These functions have no angular dependence, so that it was possible to use only one vector from each set of neighbors in the reciprocal lattice. This could also have been done for the other integrals, but the gain in computer time would have been very little, since more integrals would have had to be computed for each term in the series.

The Fourier series was summed until each integral had converged to three significant figures. The Fourier series for the potential converged very slowly; a sum over 30,000 positive vectors in the reciprocal lattice yielded two place convergence at best and for many values of r it did not converge to even one place. The integrals contained a factor of $\exp(-Kr)$ divided by K^n, where n varied from one integral to another, which made the Fourier series for the integrals converge much more rapidly. For all integrals involving p and d functions, the sum

was carried through the first 92 positive vectors, which covered 28 sets of neighbors. For integrals involving two s functions, the sum was carried out through 53 sets of neighbors. Even this did not produce convergence in the low lying s states, but functions representing these states had almost no overlap, so that the final result was unaffected by this lack of convergence. Table I contains a list of the first 53 reciprocal lattice vectors and the corresponding Fourier coefficients of potential and exchange for the assumed configuration $3d^4 4s^1$. The first 28 of these are the values over which p and d integrals were summed, although all positive permutations of K_x, K_y, K_z were used.

For the case in which both functions were located on the same site, the factor exp (-k r) disappeared, and convergence was much slower. For d - d integrals, for example, it was necessary to sum 4000 positive vectors to obtain three place convergence in the potential, although exchange converged faster than this. For s - s integrals, 15,000 terms were included in the series. This yielded convergence only for the 4s - 4s integral. The sum was extended to 30,000 terms in one case, but the integrals of core functions still did not converge.

Convergence for these central cell sums was checked not only by comparing results of successive partial sums but by comparing the result to the Hartree - Fock atomic energies. For the core states the two numbers should be very close. Since this was not the case for most integrals, the Hartree - Fock energy was used instead of the Fourier series sum for all central cell integrals except 4s, 3d, and 3p vanadium and 2p and 2s oxygen. In these latter sums the exchange potential played a major role, indicating that the Hartree - Fock energy would have been a poor approximation, since it does not permit the energy to

vary as λ changes. Table II contains the values used for various central cell integrals. For those integrals where the Hartree - Fock energy was not used, contributions from potential plus kinetic energy and exchange are listed separately. The exchange parameter for these results is equal to 1.

The sum over direct lattice vectors was carried out until each matrix element had converged to three significant figures. In some cases the convergence was better than this. The 4s - 4s matrix element required 32 terms in the direct lattice sum before convergence was obtained. All matrix elements were summed through at least eighth neighbor contributions, although this was unnecessary for the core states. The programs for calculating the three-center integrals were set up in such a way that all integrals involving functions of the same symmetry from the same atom were computed at the same time. For example, the same program which computed 3p - 3p integrals for two vanadium p functions also computed 3p - 2p and 2p - 2p integrals. Therefore the core states were carried through the same number of neighbors as were the higher functions of the same symmetry.

In order to give some idea of the extension of some of the more important wave functions, values for potential plus kinetic energy, exchange, and overlap integrals for some of the functions are given. Table III lists these values for the independent parameters for the 3d - 3d integrals through 4 neighbors. This was enough to give convergence in the eigenvalues, although not in the matrix elements. This table does not include the two central cell parameters, which were given in Table II. Table IV gives the independent parameters for the 2p - 2p integrals of oxygen through fourth neighbors, once again omitting the

central cell result. Table V gives potential plus kinetic energy, exchange and overlap for 4s - 4s integrals through 32 neighbors.

In doing integrals where both functions were centered on the oxygen sublattice, a change of variable was made to place the oxygen atom at the origin. This moved the potential to the site (a/2, 0, 0). Therefore oxygen-oxygen integrals appear to have the same coordinates as vanadium-vanadium integrals. This greatly simplified the computation of matrix elements. A similar change of variable was made so that oxygen-vanadium and vanadium-oxygen integrals use the same set of coordinates.

In the following chapter the results of the calculations described here will be presented. We now proceed to a discussion of those results.

CHAPTER IV

In this chapter the results of the energy band calculation will be given. The effects of including core states will be examined, and an attempt will be made to estimate the configuration of a self-consistent potential.

Wave functions used in this calculation were generated by Clementi (1965) for the atomic configuration $3d^3 4s^2$ for vanadium and $2p^4$ for oxygen. We were interested in the configuration $3d^4 4s^1 2p^4$ as a starting point for finding the energy band structure in the solid, so the occupation numbers were changed accordingly. Using these wave functions, we proceeded by means already described to calculate the energy band structure shown graphically in Figure 1. The notation for the irreducible representations is that of Bouckaert, Smoluchowski, and Wigner (1936).

Only the bands within 0.5 Rydbergs of the Fermi energy are depicted. These arise primarily from the 3d levels of vanadium. For example, at the maximum of bands Δ_1 and Δ_5, the band Δ_1 is about 30 per cent s and 10 per cent p, the rest being 3d, and the Δ_5 band is about 15 per cent p and 85 per cent 3d. A band arising from the 4s level of vanadium appears in the vicinity of Γ, but it quickly rises above the 3d bands. A set of bands which are due to the 2p levels of oxygen lie approximately 1.2 Rydbergs below the Fermi energy and have a width of about 2.6 ev.

Maximum width for the d bands is about 7.3 ev, with the minimum occurring at X_3 and the maximum occurring halfway along the upper Q_1 band between W and L. The energy bands along the Δ axis lie substantially lower than those along other symmetry axes, with the result that

the Fermi level lies above both Γ_{12} and Γ_{25}', although vanadium has only three 3d electrons per cation in this band picture. One of the 3d electrons and the 4s electron have been used to fill the p bands arising from oxygen.

The energy bands which have been described were computed for $\lambda = 1$; that is, using the full Slater exchange. A band structure was also calculated using $\lambda = 0.85$, a value which was suggested by Callaway and Zhang (1969) for nickel. This led to a band structure which had a positive Fermi energy, so we will confine our discussion to the energy bands computed using the full Slater exchange, at least for this configuration.

One of the things of interest about this calculation is that it is the first tight binding calculation on an element this high in the periodic table to include all the core electrons explicitly. Therefore it will be worthwhile to consider the effect of including the core states.

The band structure found from a calculation using the d bands alone is pictured along the Δ axis in Figure 2(a). They are the typical transition metal d bands, closely resembling those found for nickel in an earlier calculation (Tyler et al., 1969). Total band width is about 9.7 ev, which is rather large for a transition metal. With no core states, the Δ_1 band sweeps far down, and the Δ_5 band lies almost entirely below the Δ_2 band.

When we included the 2p states from oxygen and the 4s state from vanadium, the band structure shown in Figure 2(b) was found. The Δ_1 band has hybridized with the 4s band, and the p bands lie below the d bands in about the same position and with the same shape as in the full calculation. It is clear that at least the s states of vanadium must be added to prevent the 4s band from falling back into the core as

it approaches X. The approximation of treating the Bloch functions formed from core states as being orthogonal to those formed from conduction states is not justified here.

In Figure 3 the band structure is given in which all core states except the s states of oxygen were added. The 4s band now begins at -1.5 Rydbergs and passes up through the d bands, causing the s-d hybridization shown. It still contains a downward curve in the vicinity of X, but the X_1 point of the 4s band lies well above the Fermi energy, which is very slightly above Γ_{25}' . The Δ_5 band has been pushed above the Δ_2 band for most of the distance between Γ and X.

Comparison of this figure with Figure 1 shows the large effect produced by including the oxygen s states. Their inclusion pushed the 4s band completely above the Fermi energy, so that it plays no role in the ground state conduction picture. The Δ_1 band of the d bands now lies completely above the Δ_5 band and the Fermi energy lies above both Γ_{12} and Γ_{25}' .

From the preceding discussion it is clear that in order to obtain an accurate picture of the band structure, it is necessary to include the core states. The calculation was greatly helped in this regard by the fact that Clementi's wave functions use a single set of Slater orbitals to represent all s states from one atom and another single set to represent all p states from one atom, changing only the coefficients in going from 2p to 3p and likewise for s states. This meant that it was possible to obtain all vanadium s-s integrals, for example, by doing a single set of integrals and then combining them by using the various sets of coefficients.

In Figure 4 we have a graphical representation of the density of states near the Fermi energy for the band structure of Figure 1. This exhibits a peak above the Fermi energy arising from the flat Z_2 band of Figure 1, which is a characteristic of the face-centered cubic structure. The density of states curve is based on a sampling of 505 points in 1/48 of the Brillouin zone, as shown in Figure 5. The energy grid used was 0.008 Rydbergs.

A second band structure was calculated using the atomic configuration $3d^3 4s^2 2p^4$ as a starting point. This is the atomic configuration actually described by the wave functions. Results of this calculation along the Δ axis are shown in Figure 6(a) for the full Slater exchange.

The Fermi energy has decreased from -0.283 Rydbergs in the $3d^4 4s^1 2p^4$ configuration to -1.15 Rydbergs in this configuration. The d bands were shifted downward more than the 4s bands, and the 2p bands of oxygen lay about 0.8 Rydbergs below the Fermi energy as compared to 1.2 Rydbergs before. Final configuration for the solid in both calculations was $3d^3 4s^0 2p^6$. Ordering of bands was the same in all cases for the two calculations.

Band structures were also run for this configuration using other values of λ. For $\lambda = 0.85$, a set of bands very similar in appearance but having Fermi energy -0.77 Rydbergs was obtained, as shown in Figure 6(b). Results for the Kohn-Sham (1965) value of 2/3 for λ are shown in Figure 6(c). Fermi energy has risen to -0.304 Rydbergs. In this latter case, the point W_2' was above the point W_3 (see Figure 1). Otherwise no changes in ordering were found for either $\lambda = 0.85$ or $\lambda = 2/3$.

Comparison of the results for the different values of λ gives a picture of the effect of varying the exchange potential. With less

exchange the energy of the system is higher, of course. Since exchange affects all the d bands by approximately the same amount, changing the value of λ shifts all the d bands about the same, with the result that the overall shape and relative positions of bands tend to remain unchanged. This is evident from the three graphs in Figure 6.

A decrease in the exchange potential means that the crystal field will have a more powerful role in the structure of the bands. This is evidenced by the fact that the band splitting at the Γ point increases with decreasing λ. Band width also increases with decreasing λ. Total band width for the structure of Figure 6(a) is 7.04 ev, for that of Figure 6(b) is 8.4 ev, and for that of Figure 6(c) is 10.0 ev. For the configuration $3d^4 4s^1 2p^4$, the band width was 7.3 ev, as mentioned before.

In all respects other than those mentioned above, the bands obtained for the configuration $3d^3 4s^2 2p^4$ were very similar to those obtained for the configuration $3d^4 4s^1 2p^4$. Therefore they will not be discussed further. Instead we will turn our attention to the problem of self-consistency.

The fact that the crystal potential was formed from a superposition of spherically symmetric potentials might affect the accuracy of the crystal field splitting

$$\Delta E = E_{x^2-y^2,x^2-y^2}(000) - E_{xy,xy}(000) \quad .$$

Since there have been no other energy band calculations on VO, it is impossible to make any comparisons here. To best insure that the potential does yield the correct splitting, the band calculation should be done by a self-consistent technique. A procedure for this is now being

developed but is not yet available.

However, it would be useful to obtain at least an estimate of the self-consistent configuration. Both band structures computed at this point have seemed to indicate that the crystal contains doubly ionized atoms. Therefore it was decided to calculate another band structure using the assumed atomic configuration $3d^3 4s^0 2p^6$. The same wave functions were used; only the occupation numbers were changed.

The fact that the individual atoms were no longer neutral caused difficulties with the Fourier series convergence. The various central cell integrals were summed to convergence, taking an average of fifty per cent more Fourier coefficients than were used in the first two calculations. Other integrals, however, were summed using the same number of terms as before, with the result that convergence was probably not as good as before. Since the central cell results dominate all other contributions except in the case of the 4s band, this lack of convergence should have little effect. The 4s band lies well above the other bands, so that slight errors in it should not be felt in the vicinity of the Fermi energy.

The band structure obtained for this configuration is shown along the Δ and Z axes in Figure 7. This structure is based on the full Slater exchange. The p bands have been raised above the d bands and are completely empty. Electronic configuration for these bands is $3d^9 4s^0 2p^0$. This result seems to indicate that the crystal cannot be treated as being doubly ionized.

Before going on to discuss the problem of self-consistency further, it would be appropriate to digress to make a comparison of this last band calculation to one done by Yamashita (1963) for titanium monoxide (TiO).

The TiO calculation also used wave functions based on a doubly ionized configuration for the atom. His method was the tight binding approximation as modified by Stern (1959), in which the radial equation is solved numerically in two cells, one centered on titanium and the other on oxygen. His calculation included no exchange, and core functions were not explicitly included. Also, interactions among s, d, and p electrons were not included.

He found the 2p bands lying below the d bands with a band width of 10.7 ev. He calculated values only at the points Γ, X, and L, so his band width result is the maximum spread at those points. These results are in opposition to the results of our calculation. In our case the width of the p bands is difficult to determine since there is a great deal of p-d interaction. However, it is about 3 ev. The difference in results for the two cases is probably due to the differences in method which were mentioned. There is also the fact that in Yamashita's calculations the 2p atomic orbital used was probably inaccurate. He was mainly interested in d bands, and so made little effort to obtain accurate results for the p bands.

We will now return to the problem of the consistency of the calculation. Our goal here is to obtain an estimate of the self-consistent configuration. This is done by the procedure described below.

All three calculations have given an empty 4s band as the final result. Therefore the nine electrons must be spread between the 3d and 2p bands. Since the p levels will not be fully occupied, they must lie very close to the d levels in order to have some portion above the Fermi energy. Therefore we seek a configuration in which the Γ_{15} point lies very close to the Γ'_{25} point. Evidently some small adjustment to the

$3d^3 4s^0 2p^6$ configuration should yield the correct answer.

In order to compute this adjustment, we need to know the effect on relative positions of bands of moving electrons from the p band to the d band. This can be found by examining the s-d, p-d, and s-p energy gaps at Γ for each of the three configurations used so far. One can determine the effect on relative band positions of moving two s electrons to the p bands by considering the difference between energy gaps for the configurations $3d^3 4s^2 2p^4$ and $3d^3 4s^0 2p^6$. Assuming that the effect of moving one electron from 4s to 2p is half this, it was found that changing one electron from s to p raised the 4s band relative to the 3d band by 0.186 Rydbergs, raised the 2p band relative to the 3d band by 0.52 Rydbergs, and raised the 2p band relative to the 4s band by 0.375 Rydbergs. Comparison of the energy gaps for the configurations $3d^4 4s^1 2p^4$ and $3d^3 4s^0 2p^6$ allowed us to determine the effect of removing an electron from the 3d band and placing it in the 2p band, if it is assumed that the effect of transferring a 4s and a 3d electron simultaneously to 2p is equal to the sum of the individual effects. From this we found that transferring an electron from 3d to 2p raises the 4s band relative to the 3d band by 0.81 Rydbergs, raises the 2p band relative to the 3d band by 1.02 Rydbergs, and lowers the 4s band relative to the 2p band by 0.285 Rydbergs.

Since the energy gap between Γ_{15} and Γ'_{25} for the configuration $3d^3 4s^0 2p^6$ was 0.325 Rydbergs, we concluded from the above that a transfer of about 0.3 electrons from the 2p band to the 3d band would bring p and d bands at Γ into close proximity, which is what we desired. The conclusion was therefore that an approximately self-consistent potential for VO is $3d^{3.3} 4s^0 2p^{5.7}$.

It should be pointed out here that self-consistency is determined not by the configuration but by the crystalline charge density. In a calculation on TiO by Ern and Switendick (1965) for example, the initial atomic configuration assumed was $3d^2 4s^1 2p^5$, while the apparent equivalent configuration for the band electrons was $3d^2 4s^0 2p^6$. However, the charge densities, as plotted in the spheres centered on titanium and oxygen, were very nearly the same. Thus comparing configurations may be misleading. An accurate determination of the degree of self-consistency can be made only by comparing charge densities obtained from successive band calculations computed in some sort of iterative procedure.

CHAPTER V

In this final chapter, we will briefly discuss the possibility of a metal-insulator transition in VO, compare the results of this calculation to those of a calculation on TiO, and suggest certain improvements which could be made in future investigations.

The possibility of a metal-insulator transition in VO due to the onset of antiferromagnetic order was presented by Morin in 1959, when he first reported a transition in VO, and later discussed by Adler (1968) after the work of Warren et al. (1967), although Adler assumed a simultaneous crystalline distortion. One of the requirements for a transition caused by antiferromagnetic splitting of the bands is that there be little or no overlap between Γ_{12} bands and Γ_{25}' bands. Otherwise no gap can be introduced. From Figure 1 it is evident that this criterion is not satisfied in VO. It is more difficult to assess the possibility of a transition caused by crystalline distortion, since band splitting and even the ordering of bands could not be determined without knowing the low temperature structure of VO. However, due to the relatively large band width of the bands arising from Γ_{25}', a transition of this type appears unlikely. Further discussion of this topic must wait until the question of the existence of the transition has been settled.

An APW calculation of the energy bands of TiO was performed by Ern and Switendick (1965), who assumed the atomic configuration $3d^2 4s^1 2p^5$, which corresponds to singly ionized atoms. They found the 2p bands from oxygen to lie 0.35 Rydbergs below the 3d bands at Γ. Based on the interpolation procedure described at the end of Chapter IV, the 2p bands of oxygen would be 0.2 Rydbergs below the 3d bands at Γ

for a calculation on VO using singly ionized atoms. Total band width for TiO was found to be about 9 ev, compared to about 7 ev in VO. It is to be expected that the band width in TiO is larger than in VO, since TiO is a better metal and lies further to the left in the transition series.

The conduction in VO is due mainly to the 3d bands, based on the estimate of a self-consistent potential made in Chapter IV. According to that estimate, there would be a small pocket of holes somewhere on the Fermi surface due to the 2p bands of oxygen. This pocket should contain only 0.3 holes, so that the 3d bands will dominate the Fermi surface features. This can be determined definitely only by a self-consistent calculation.

The calculation can be improved in several ways. First, of course, it should be done self-consistently by a systematic process in which each calculation begins with the results of the previous one. This will be done in the near future. A second correction which would be useful is to include more conduction band states, such as a 4p from vanadium and 3s from oxygen. This would no doubt have the effect of repelling some of the higher 3d bands and thus narrowing the band width. Minimum band width possible is about 6.9 ev, since the points L_3 and X_3 are unaffected by s and p bands. Finally, if one wishes to make detailed studies of the Fermi surface, the effects of spin-orbit coupling should be included. There appears to be little value in this at the present time,however. Even if VO is a metal at the temperatures for which Fermi surface measurements are made, it is so highly defective that the mean free path of electrons is probably too short to obtain good results. Since very little is known about VO experimentally, we have not tried to

predict anything other than its gross properties from the band calculation.

We conclude this discussion of results by estimating the overall accuracy of this calculation. In carrying out the various sums and integrations involved in the calculation, we attempted to achieve at least three figure accuracy in each. Allowing for some loss of accuracy in carrying out the computations, it is estimated that the results quoted for the energy bands are accurate within 0.02 Rydbergs, which certainly would not cause any reordering of bands due to numerical errors. As mentioned before, the calculation for the ionic case was not as accurate as the others, although we believe any errors would be small.

Finally, we would like to mention a very important practical consideration in the use of this method to compute energy bands. Computer time on an IBM 360-65 for the first band structure was about 60 hours. Successive iterations require only four to five hours, since the basic integrals can be stored on tape and reused provided the Slater orbitals are not changed. Refinements in technique should permit both the initial time and time for the iterations to be reduced considerably in the future. For future reference we have included three-center programs used in this calculation as Appendix C. The programs are commented with explanations to facilitate usage, and are written in Fortran IV.

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TABLE I

RECIPROCAL LATTICE VECTOR	FOURIER COEFFICIENT OF POTENTIAL	FOURIER COEFFICIENT OF EXCHANGE
000	-1.7134 RYDBERGS	-0.93112 RYDBERGS
111	-0.35346	-0.061622
200	-0.83970	-0.37232
220	-0.60412	-0.10930
131	-0.19506	-0.016291
222	-0.47470	-0.0068919
400	-0.39046	0.016495
331	-0.14030	-0.0045957
240	-0.33097	0.0074661
422	-0.28676	-0.0094525
333	-0.10902	-0.0031780
511	-0.10902	-0.0031780
440	-0.22577	-0.029806
531	-0.088932	-0.0036546
600	-0.20397	-0.029922
442	-0.20397	-0.029922
620	-0.18602	-0.025360
335	-0.075128	-0.0037931
622	-0.17100	-0.018407
444	-0.15827	-0.011053
551	-0.065154	-0.0034620
711	-0.065154	-0.0034620
640	-0.14736	-0.0047153

TABLE I (Cont.)

264	-0.13792	-0.00020310
137	-0.05[illegible]	-0.0029812
553	-0.057655	-0.0029812
800	-0.12239	0.0026204
733	-0.051832	-0.0025842
820	-0.11594	0.0014205
644	-0.11594	0.0014205
228	-0.11018	-0.00089478
660	-0.11018	-0.00089478
715	-0.047186	-0.0023371
555	-0.047186	-0.0023371
662	-0.10500	-0.0037961
840	-0.10032	-0.0067985
119	-0.043391	-0.0021985
537	-0.043391	-0.0021985
284	-0.096075	-0.0095067
664	-0.092201	-0.011638
391	-0.040229	-0.0020945
844	-0.085388	-0.013605
933	-0.037549	-0.0019663
755	-0.037549	-0.0019663
771	-0.037549	-0.0019663
860	-0.082376	-0.013412
0010	-0.082376	-0.013412
862	-0.079585	-0.012541

TABLE I (Cont.)

0210	-0.079585	-0.012541
159	-0.035244	-0.0017875
773	-0.035244	-0.0017875
2210	-0.076993	-0.011138
666	-0.076993	-0.011138

TABLE II

	HARTREE-FOCK ATOMIC ENERGY (RYDBERGS)	POTENTIAL + K.E. (RYDBERGS)	EXCHANGE (RYDBERGS)
1s-1s(V)	-403.004		
2s-2s(V)	- 47.7485		
3s-3s(V)	- 6.36626		
$2p_x$-$2p_x$(V)	- 40.0441		
1s-1s(0)	- 41.3864		
$3p_x$-$3p_x$(V)		-0.66111	-3.0408
$3d_{xy}$-$3d_{xy}$(V)		1.9921	-2.38687
$3d_{x^2-y^2}$-$3d_{x^2-y^2}$(V)		1.9340	-2.4687
4s-4s(V)		-0.73614	-0.85674
2s-2s(0)		-0.45890	-1.940
$2p_x$-$2p_x$(0)		-0.3096	

TABLE III

INTEGRAL	NEIGHBOR	POTENTIAL + K.E. (RYDBERGS)	EXCHANGE (RYDBERGS)	OVERLAP
xy,xy	110	-0.013533	-0.018263	0.028805
xz,xz	110	0.014814	0.0055322	-0.11041
yz,xz	110	0.022171	0.010374	-0.017641
x^2-y^2,x^2-y^2	110	0.054771	0.032921	-0.28683
$3z^2-r^2,3z^2-r^2$	110	-0.014825	-0.14572	0.14001
$xy,2z^2-r^2$	110	0.0050073	0.010396	-0.12820
xy,xy	002	0.0008587	-0.0004164	0.0007628
xz,xz	002	0.056684	0.0035288	-0.0047653
x^2-y^2,x^2-y^2	002	-0.0016500	-0.0008252	0.76283
$3z^2-r^2,3z^2-r^2$	002	-0.016694	-0.011154	0.0086867
xy,xy	112	-0.0001643	-0.0000274	0.00007008
xz,xz	112	-0.0006314	-0.0002646	0.0004947
xy,xz	112	-0.0003091	-0.0001569	0.0002831
yz,xz	112	-0.0018143	-0.0009518	0.0012314
x^2-y^2,x^2-y^2	112	0.0005365	0.0003374	-0.0002932
$3z^2-r^2,3z^2-r^2$	112	-0.0000445	0.0001120	-0.0000904
$xy,3z^2-r^2$	112	-0.0013379	-0.0008810	0.0008853
$yz,3z^2-r^2$	112	-0.0016076	-0.0009911	0.0010024
$xz,3z^2-r^2$	112	0.0007762	0.0004628	-0.0004435
xy,xy	220	-0.0015149	-0.0006727	0.0007453
xz,xz	220	0.0001228	0.0001079	-0.0001577
yz,xz	220	0.0001935	0.0001388	-0.0001958
x^2-y^2,x^2-y^2	220	0.0004439	0.0003498	-0.0003535

TABLE III (Cont.)

$3z^2-r^2, 3z^2-r^2$	220	-0.0006258	-0.0003070	0.0002738
$xy, 3z^2-r^2$	220	0.0009194	0.0004428	-0.0004083

TABLE IV

INTEGRAL	NEIGHBOR	POTENTIAL + K.E. (RYDBERGS)	EXCHANGE (RYDBERGS)	OVERLAP
$2p_x\ 2p_x$	110	0.020731	0.015933	-0.020321
$2p_z\ 2p_z$	110	-0.017555	-0.0092185	0.012889
$2p_y\ 2p_x$	110	0.051565	0.031263	-0.033211
$2p_x\ 2p_x$	002	-0.0025728	-0.0012367	0.0015517
$2p_z\ 2p_z$	002	0.019164	0.011193	-0.0095615
$2p_x\ 2p_x$	112	-0.00016994	0.00008054	-0.0001403
$2p_z\ 2p_z$	112	0.0016397	0.0013462	-0.0015002
$2p_y\ 2p_x$	112	0.00046009	0.0003718	-0.0004533
$2p_y\ 2p_z$	112	0.0010286	0.0007598	-0.0009066
$2p_x\ 2p_x$	220	0.00030285	0.0002958	-0.0003275
$2p_z\ 2p_z$	220	-0.00015390	-0.00006415	0.00008174
$2p_y\ 2p_x$	220	0.00051499	0.0003836	-0.0004093

TABLE V

NEIGHBOR	POTENTIAL + K.E. (RYDBERGS)	EXCHANGE (RYDBERGS)	OVERLAP
110	-0.52091	-0.33517	0.45595
002	-0.33492	-0.19396	0.23305
112	-0.19270	-0.10488	0.12211
220	-0.11210	-0.058653	0.066344
310	-0.064740	-0.033453	0.037266
222	-0.038270	-0.019375	0.021560
321	-0.023260	-0.011616	0.012807
004	-0.014292	-0.0070803	0.0077897
114	-0.0089598	-0.0044028	0.0048412
330	-0.0090094	-0.0044136	0.0048412
420	-0.0057236	-0.0028033	0.0030685
332	-0.0037135	-0.0018078	0.0019804
224	-0.0024475	-0.0011869	0.0012995
431	-0.0016399	-0.0007928	0.0008659
510	-0.0016381	-0.0007935	0.0008659
521	-0.0007623	-0.0003675	0.0004008
440	-0.0005298	-0.0002546	0.0002778
334	-0.0003713	-0.0001784	0.0001947
530	-0.0003717	-0.0001786	0.0001947
442	-0.0002635	-0.0001265	0.0001379
006	-0.0002632	-0.0001265	0.0001379
532	-0.0001888	-0.0000905	0.0000986
116	-0.0001884	-0.0000905	0.0000986

TABLE V (Cont.)

026	-0.0001362	-0.0000653	0.0000712
541	-0.0000993	-0.0000476	0.0000518
226	-0.0000727	-0.0000349	0.0000380
631	-0.0000538	-0.0000258	0.0000280
444	-0.0000400	-0.0000192	0.0000209
710	-0.0000300	-0.0000144	0.0000156
543	-0.0000300	-0.0000143	0.0000156
550	-0.0000300	-0.0000143	0.0000156
640	-0.0000226	-0.0000108	0.0000118

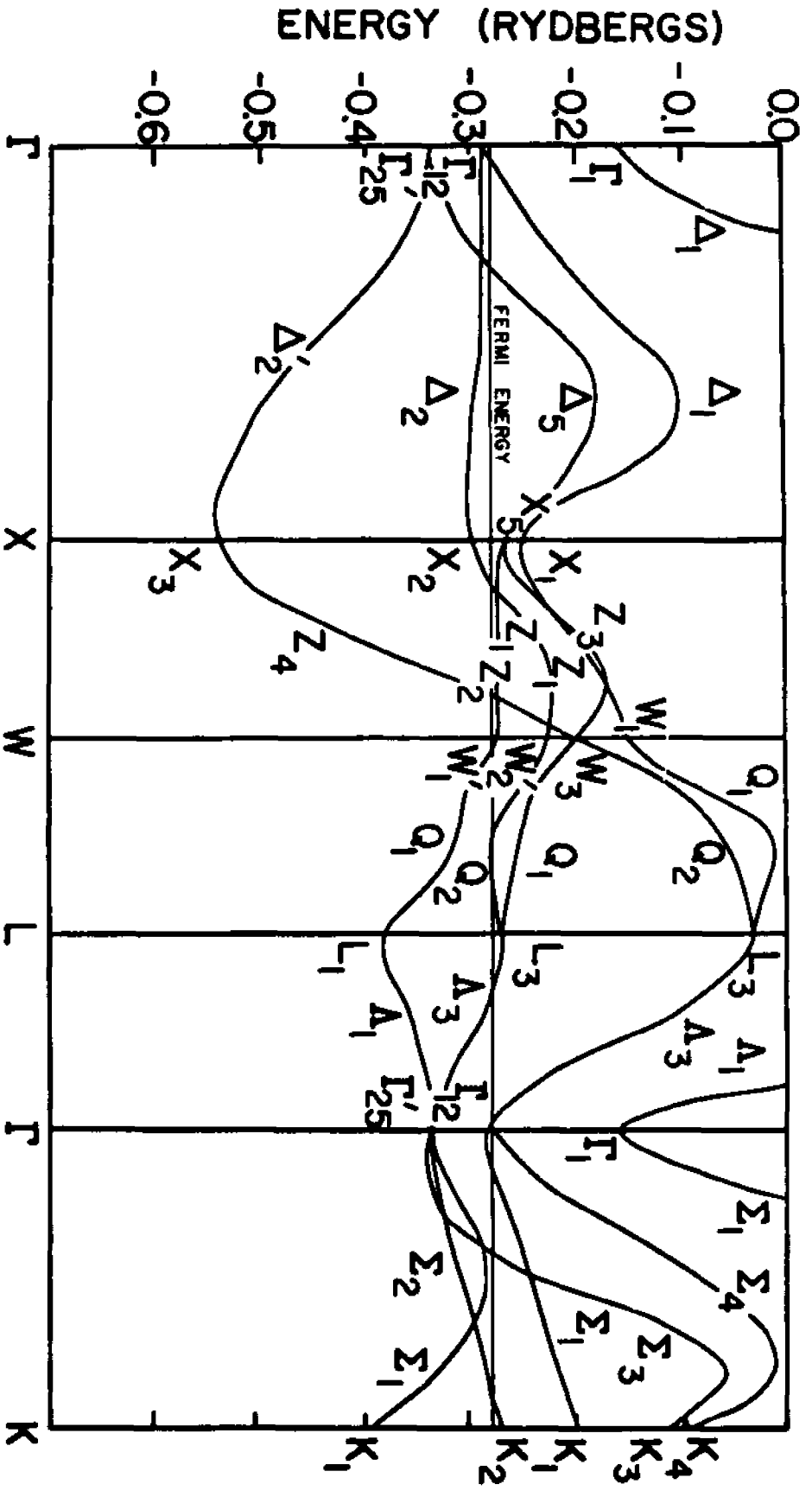

FIGURE 1

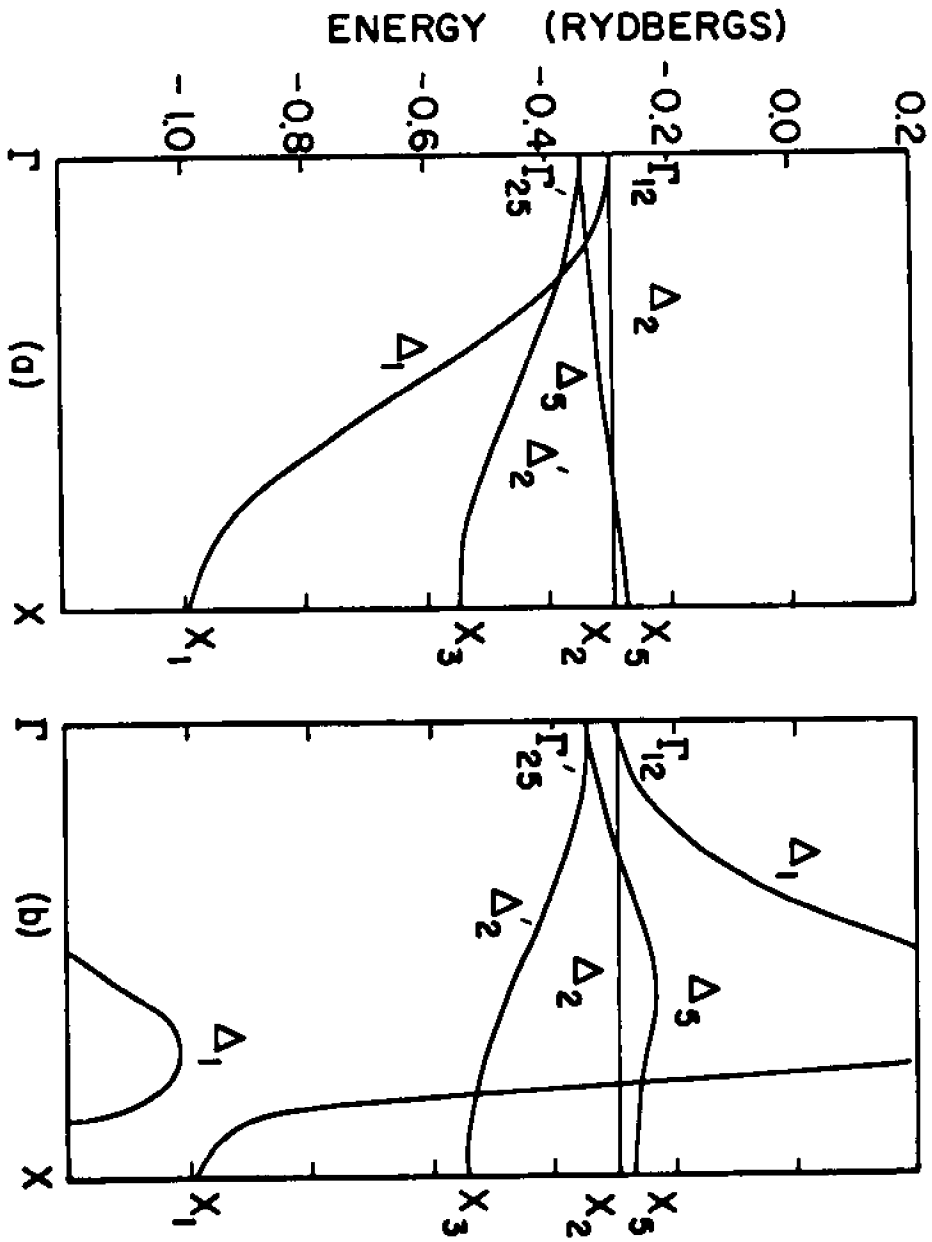
ENERGY (RYDBERGS)
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
Γ
X
(a)
Γ25'
Γ12
Δ1
Δ2
Δ5
Δ2'
X1
X3
X2
X5
Γ
X
(b)
Γ25'
Γ12
Δ1
Δ2'
Δ2
Δ5
Δ1
X1
X3
X2
X5

FIGURE 2

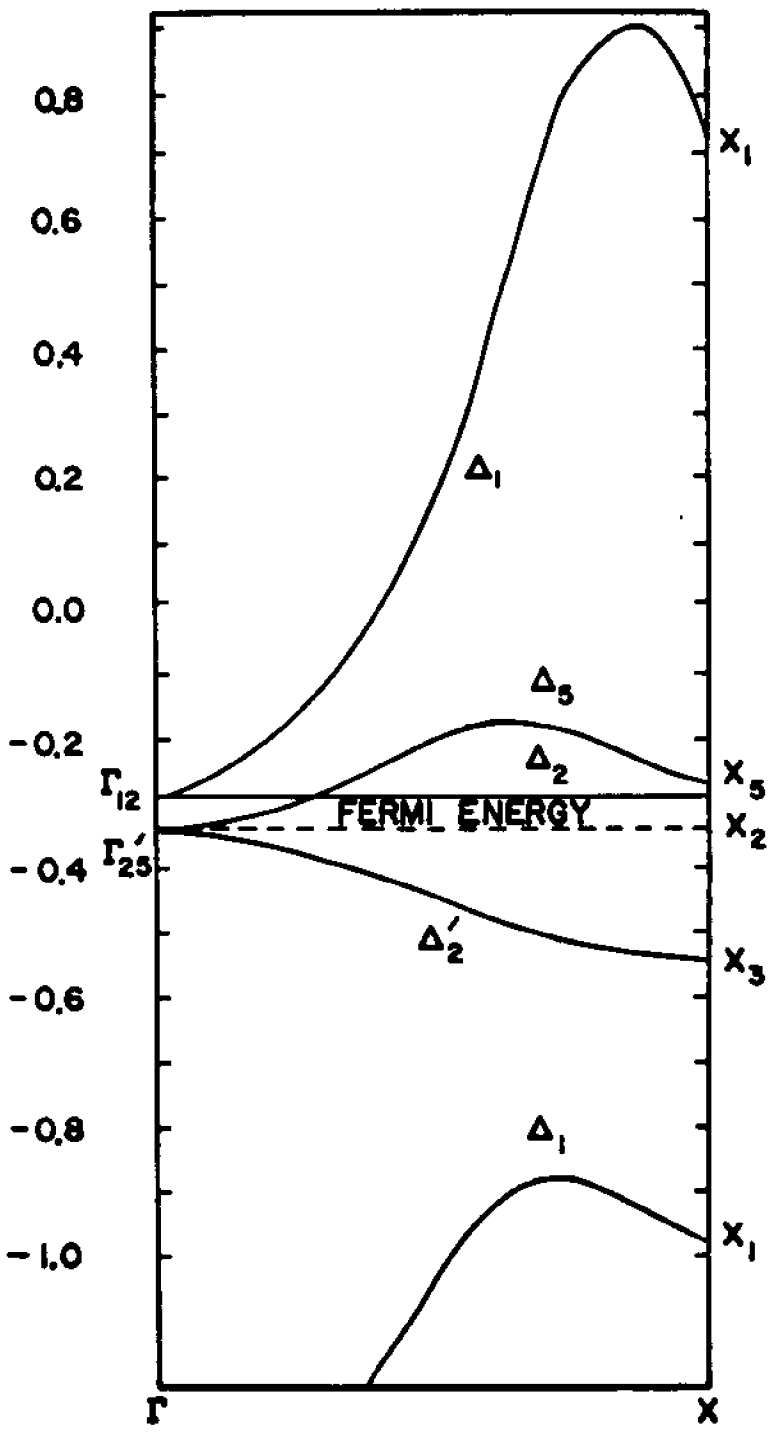
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
Γ_{12}
Γ_{25}'
Δ_1
Δ_5
Δ_2
Δ_2'
Δ_1
FERMI ENERGY
X_1
X_5
X_2
X_3
X_1
Γ
X

FIGURE 3

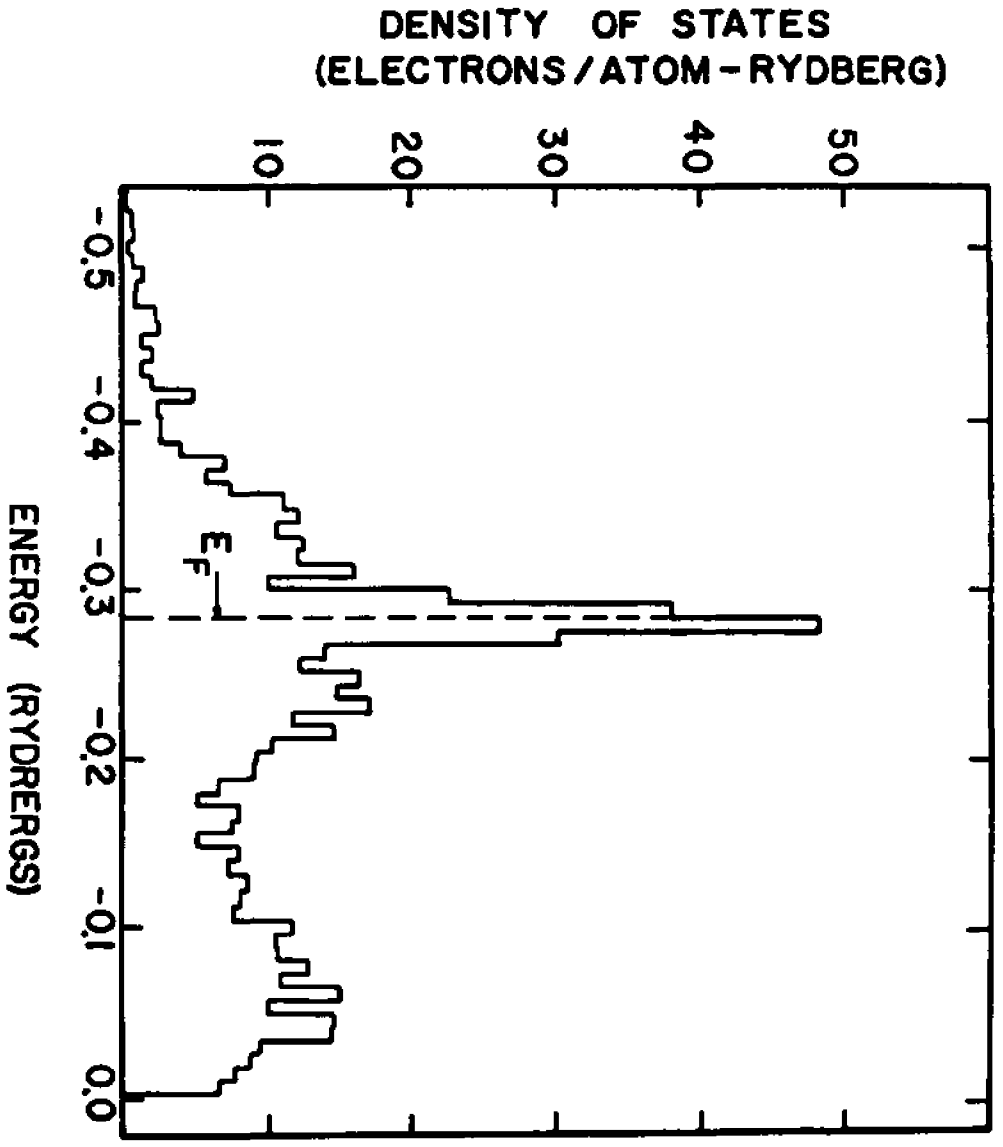
DENSITY OF STATES
(ELECTRONS / ATOM - RYDBERG)
10
20
30
40
50
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
E_F
ENERGY (RYDRERGS)

FIGURE 4

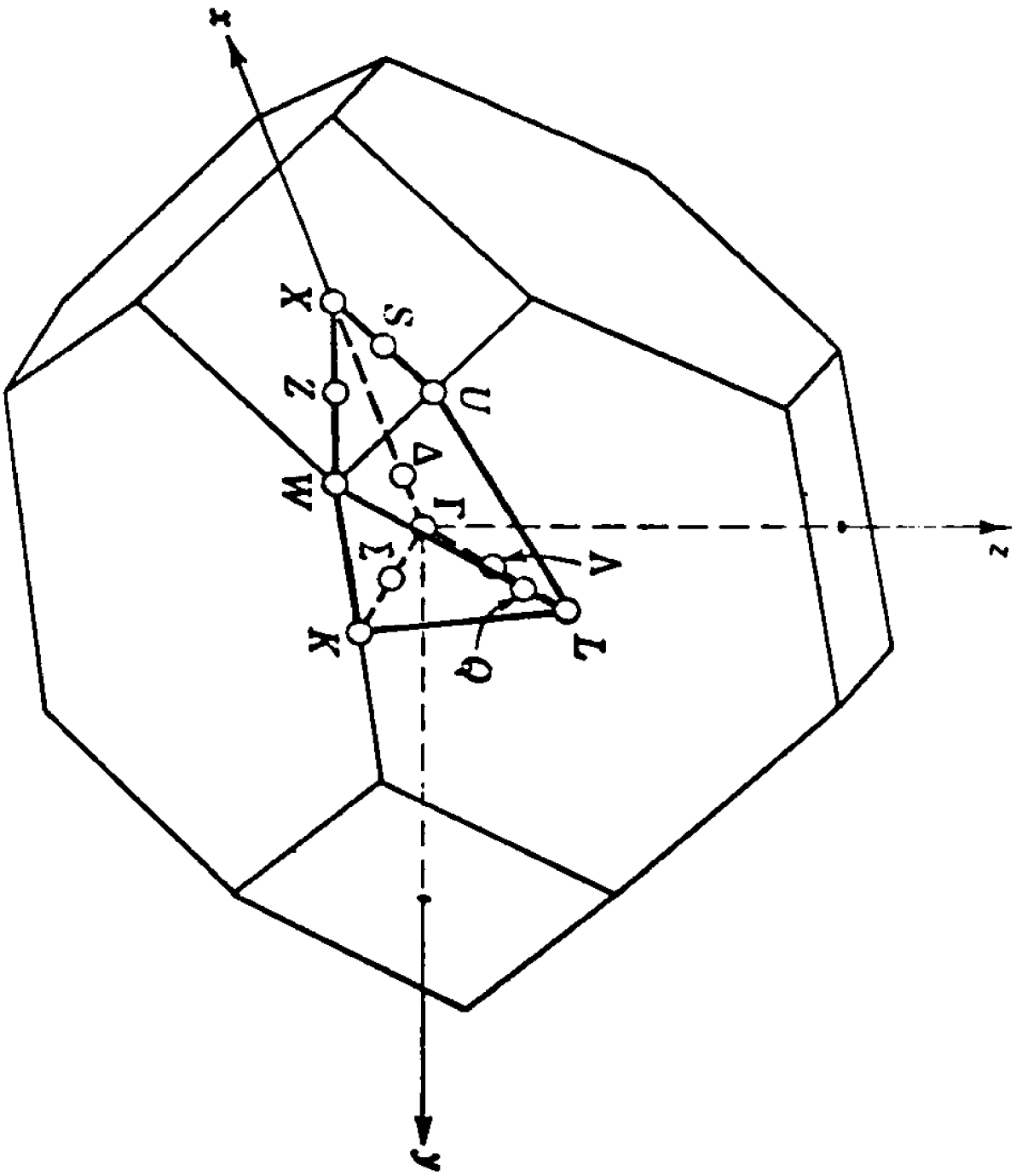

FIGURE 5

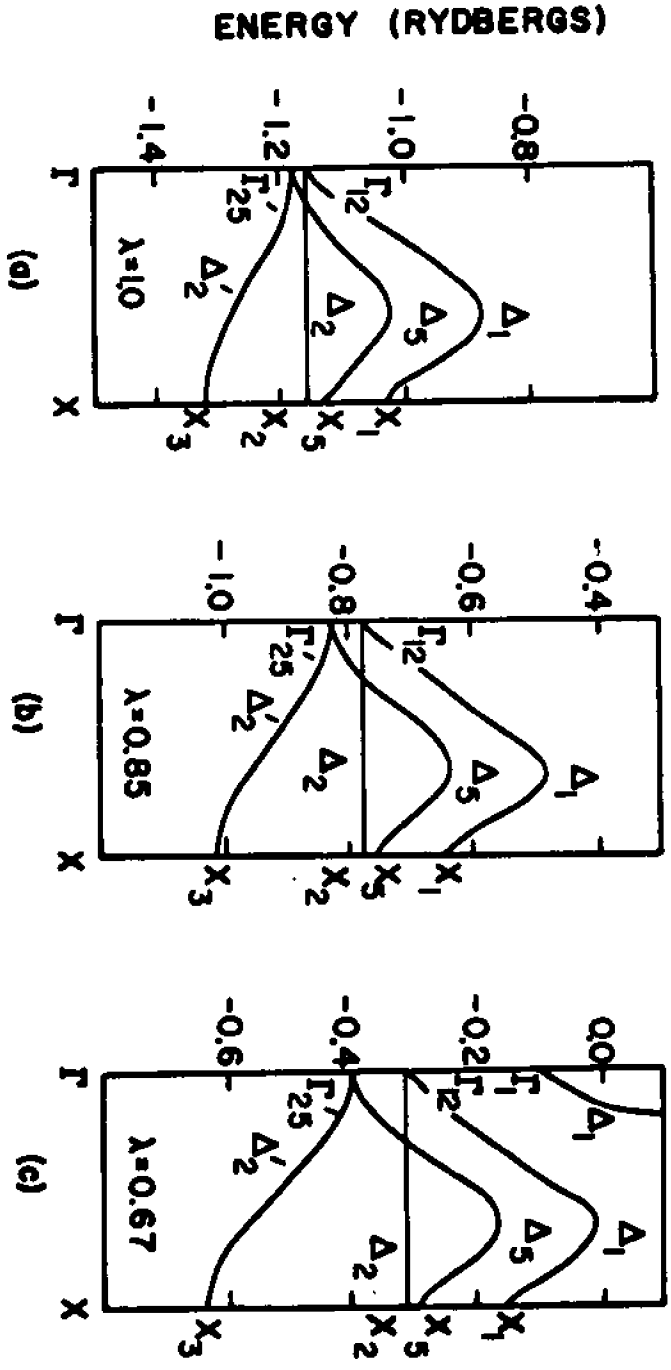
ENERGY (RYDBERGS)
-1.4
-1.2
-1.0
-0.8
Γ
X
(a)
λ=1.0
Γ'25
Γ12
Δ'2
Δ2
Δ5
Δ1
X3
X2
X5
X1
-1.0
-0.8
-0.6
-0.4
(b)
λ=0.85
-0.6
-0.4
-0.2
0.0
(c)
λ=0.67
Γ1
Γ2

FIGURE 6

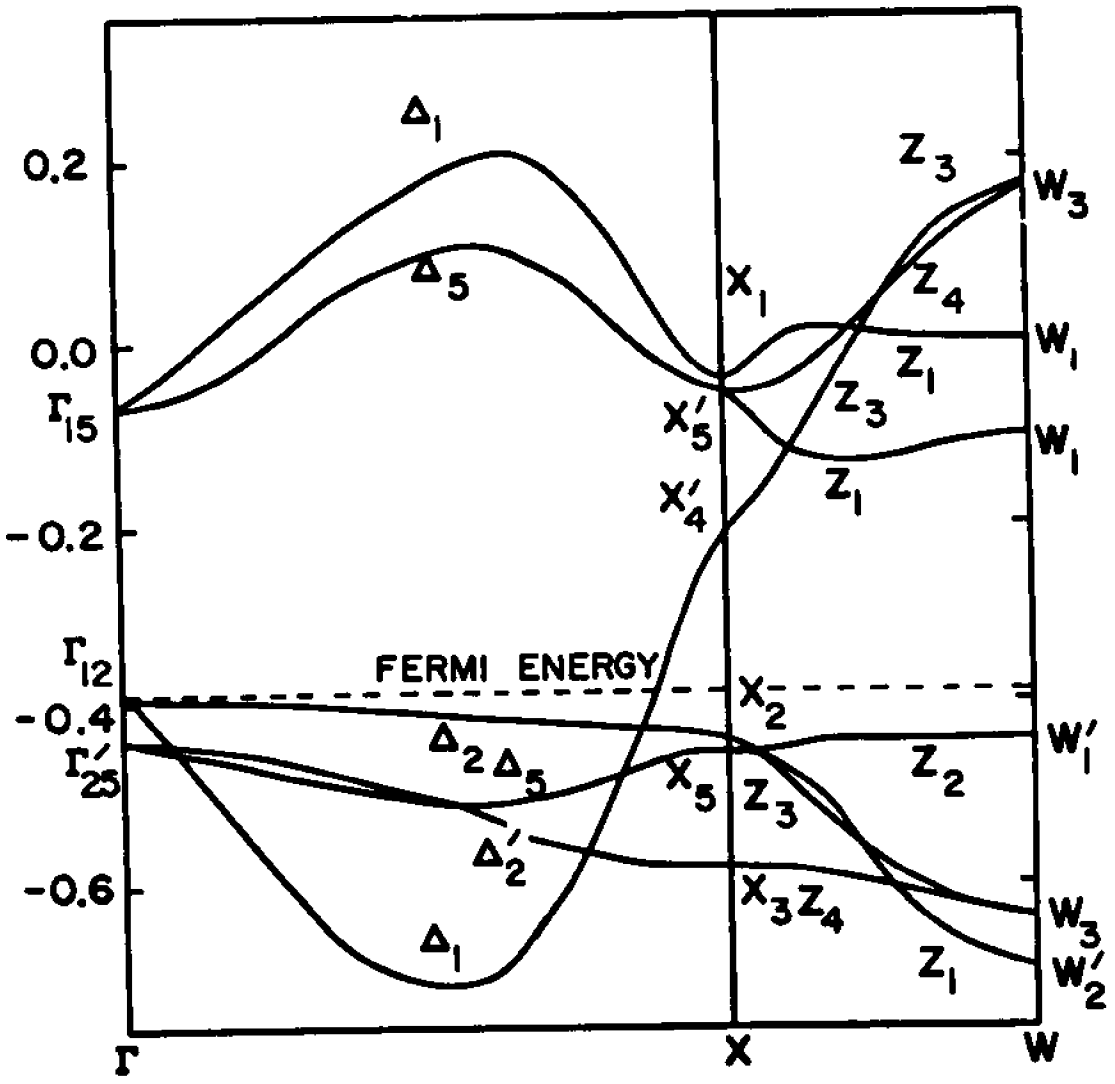
0.2
0.0
-0.2
-0.4
-0.6
Γ15
Γ12
Γ'25
FERMI ENERGY
Δ1
Δ5
Δ2 Δ5
Δ'2
Δ1
X1
X'5
X'4
X2
X5
X3 Z4
Z3
Z1
Z4
Z1
Z3
Z1
Z2
Z3
Z1
W3
W1
W1
W'1
W3
W'2
Γ
X
W

FIGURE 7

APPENDIX A

The potential integrals involving any Slater orbitals can be obtained from the 1s-1s integral given in the second chapter by taking the proper partial derivatives. These derivatives become very tedious for higher orbitals if carried out step by step. However, a set of recursion relations for the derivatives was discovered empirically, and this greatly simplifies the work. These will be presented in this appendix, together with the integrals used in this calculation. In addition to the definitions given in Chapter II, the following will be useful:

$$A(0) = \frac{1}{(fg)^{3/2}} + \frac{1}{(fg)}$$

$$A(1) = f\left[\frac{3}{(fg)^{5/2}} + \frac{3}{(fg)^{2}} + \frac{1}{(fg)^{3/2}}\right]$$

$$A(2) = f^{2}\left[\frac{15}{(fg)^{7/2}} + \frac{15}{(fg)^{3}} + \frac{6}{(fg)^{5/2}} + \frac{1}{(fg)^{2}}\right]$$

$$A(3) = f^{3}\left[\frac{105}{(fg)^{9/2}} + \frac{105}{(fg)^{4}} + \frac{45}{(fg)^{7/2}} + \frac{10}{(fg)^{3}} + \frac{1}{(fg)^{5/2}}\right]$$

$$A(4) = f^{4}\left[\frac{945}{(fg)^{11/2}} + \frac{945}{(fg)^{5}} + \frac{420}{(fg)^{9/2}} + \frac{105}{(fg)^{4}} + \frac{15}{(fg)^{7/2}} + \frac{1}{(fg)^{3}}\right]$$

$$A(5) = f^{5}\left[\frac{10395}{(fg)^{13/2}} + \frac{10395}{(fg)^{6}} + \frac{4725}{(fg)^{11/2}} + \frac{1260}{(fg)^{5}} + \frac{210}{(fg)^{9/2}} + \frac{21}{(fg)^{4}} + \frac{1}{(fg)^{7/2}}\right]$$

$$A(6) = f^6\left[\frac{135135}{(fg)^{15/2}} + \frac{135135}{(fg)^7} + \frac{62370}{(fg)^{13/2}} + \frac{17325}{(fg)^6} + \frac{3150}{(fg)^{11/2}} + \frac{378}{(fg)^5} + \frac{28}{(fg)^{9/2}} + \frac{1}{(fg)^4}\right]$$

$$A(7) = f^7\left[\frac{2027025}{(fg)^{17/2}} + \frac{2027025}{(fg)^8} + \frac{945945}{(fg)^{15/2}} + \frac{270270}{(fg)^7} + \frac{51975}{(fg)^{13/2}} + \frac{6930}{(fg)^6} + \frac{630}{(fg)^{11/2}} + \frac{36}{(fg)^5} + \frac{1}{(fg)^{9/2}}\right]$$

$\cos = \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD}$

$\sin = \sin \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD}$

$B_x - A_x = D_x \qquad (\underset{\sim}{K}_\nu)_x = K_x$

$B_y - A_y = D_y \qquad (\underset{\sim}{K}_\nu)_y = K_y$

$B_z - A_z = D_z \qquad (\underset{\sim}{K}_\nu)_z = K_z$

$C = 2\pi\alpha_1\alpha_2 r_{AB}^3 \qquad h = u(1-u)$

In terms of these quantities, the 1s-1s potential integral becomes

$$\langle 1s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C|1s(B)\rangle = C\int_0^1 \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD}\, A(1) e^{-(fg)^{\frac{1}{2}}}\, du$$

Any potential integral involving Slater-type orbitals not higher than 4s can be written in the following manner:

$$\langle \Phi_i(A) | \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C | \Phi_j(B) \rangle = \sum_{N=1}^{7} C \int_o^1 F_N \, A(N) e^{-(fg)^{\frac{1}{2}}} \, du$$

where F_N is in general a function of D_x, D_y, D_z, K_x, K_y, α_1, α_2, K_z, and u. F_N will always contain either or both of the factors $\cos K_\nu \cdot r_{CD}$, $\sin K_\nu \cdot r_{CD}$. Before giving the recursion relations for derivatives of this integral, we note the following results.

$$\frac{d}{dA_x} \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} = - K_x u \sin \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} \tag{1}$$

$$\frac{d}{dB_x} \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} = -K_x (1-u) \sin \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} \tag{2}$$

There are four derivatives of the integral in which we are interested. The results for these are now presented in equations (3) through (6).

$$\frac{d}{dA_x} \langle \Phi_i(A) | \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C | \Phi_j(B) \rangle =$$

$$\frac{d}{dA_x} \sum_{N=1}^{7} C \int_o^1 F_N \, A(N) e^{-(fg)^{\frac{1}{2}}} \, du =$$

$$\sum_{N=1}^{7} C \int_o^1 \left[D_x h \, F_N \, A(N-1) + \frac{dF_N}{dA_x} A(N) \right] e^{-(fg)^{\frac{1}{2}}} \, du \tag{3}$$

$$\frac{d}{dB_x} \langle \Phi_i(A) | \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_{CD} | \Phi_j(B) \rangle =$$

$$\sum_{N=1}^{7} C \int_o^1 \left[- D_x h \, F_N \, A(N-1) + \frac{dF_N}{dB_x} \, A(N) \right] e^{-(fg)^{\frac{1}{2}}} \, du \tag{4}$$

$$\frac{d}{d\alpha_1} \langle \Phi_i(A) | \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C | \Phi_j(B) \rangle =$$

$$\sum_{N=1}^{7} C \int_o^1 \left[\frac{1}{\alpha_1} \frac{d(\alpha_1 F_N)}{d\alpha_1} \, A(N) - \frac{\alpha_1}{u} A(N+1) \right] e^{-(fg)^{\frac{1}{2}}} \, du \tag{5}$$

$$\frac{d}{d\alpha_2} \langle \Phi_i(A) | \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C | \Phi_j(B) \rangle =$$

$$\sum_{N=1}^{7} C \int_0^1 \left[\frac{1}{\alpha_2} \frac{d(\alpha_2 F_N)}{d\alpha_2} A(N) - \frac{\alpha_2}{1-u} A(N+1) \right] e^{-(fg)^{\frac{1}{2}}} du \qquad (6)$$

The function F_N is always simple enough so that its derivatives can be easily found with the aid of equations (1) and (2). Therefore, by repeated application of equations (3), (4), (5), and (6), the potential integral between any two Slater-type orbitals can be written down with a minimum of effort, rather than the hours of tedious labor which would be required to do the partial derivatives for some of the higher orbitals.

In this paper we are not interested in orbitals higher than 4s. The method can readily be extended to treat more involved cases, although the author suspects that even this simple technique would become quite complicated in dealing with functions other than those of s, p, d, or f symmetry.

We will now list the expressions for the three-center potential integrals which were used in this calculation. Those integrals involving two functions of d symmetry have already been listed (Tyler, Norwood, and Fry, 1969) and will not be shown here. Integrals which are identical except for a permutation of coordinates will have only one member given.

S-S Integrals

$$\langle 1s(A) | \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C | 1s(B) \rangle = C \int_0^1 \cos A(1) e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2s(A) | \cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C | 1s(B) \rangle = C \int_0^1 \left[-\frac{1}{\alpha_1} A(1) + \frac{\alpha_1}{u} A(2) \right] \cos e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 3s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |1s(B)\rangle = C \int_0^1 [-\frac{3}{u} A(2) + (\frac{\alpha_1}{u})^2 A(3)] \cos\, e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 4s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |1s(B)\rangle = C \int_0^1 [\frac{3}{u\alpha_1} A(2) - \frac{6\alpha_1}{u^2} A(3) + (\frac{\alpha_1}{u})^3 A(4)] \cos\, e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |2s(B)\rangle = C \int_0^1 [(-\frac{\alpha_1}{\alpha_2 u} - \frac{\alpha_2}{\alpha_1(1-u)})A(2) + \frac{\alpha_1\alpha_2}{h} A(3)] \cos\, e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 3s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |2s(B)\rangle = C \int_0^1 [\frac{3}{\alpha_2 u} A(2) - (\frac{\alpha_1}{\alpha_2 u} + \frac{3\alpha_2}{h}) A(3) + \frac{\alpha_1^2\alpha_2}{uh} A(4)] e^{-(fg)^{\frac{1}{2}}} \cos\, du$$

$$\langle 4s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |2s(B)\rangle = C \int_0^1 [-\frac{3}{\alpha_1\alpha_2 u} A(2) + (\frac{6\alpha_1}{u^2\alpha_2} + \frac{3\alpha_2}{h\alpha_1}) A(3) - (\frac{\alpha_1^3}{\alpha_2 u^3} + \frac{6\alpha_1\alpha_2}{uh}) A(4) + \frac{\alpha_1^3\alpha_2}{u^2 h} A(5)] e^{-(fg)^{\frac{1}{2}}} \cos\, du$$

$$\langle 3s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |3s(B)\rangle = C \int_0^1 [\frac{9}{h} A(3) - (\frac{3\alpha_1^2}{uh} - \frac{3\alpha_2^2}{(1-u)h}) A(4) + \frac{\alpha_1^2\alpha_2^2}{h^2} A(5)] \cos\, e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 4s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |3s(B)\rangle = C \int_0^1 [-\frac{9}{h\alpha_1} A(3) + (\frac{18\alpha_1}{uh} + \frac{3\alpha_2^2}{\alpha_1(1-u)h} A(4) - (\frac{6\alpha_1\alpha_2^2}{h^2} + \frac{3\alpha_1^3}{u^2 h}) A(5) + \frac{\alpha_1^3\alpha_2^2}{uh^2} A(6)] \cos\, e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 4s(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|4s(B)\rangle = C\int_o^1 [\frac{9}{h\alpha_1\alpha_2}A(3) - \frac{18}{h}(\frac{\alpha_1}{\alpha_2 u} + \frac{\alpha_2}{\alpha_1(1-u)})A(4)$$
$$+ (\frac{36\alpha_1\alpha_2}{h^2} + \frac{3\alpha_2^3}{\alpha_1(1-u)^2h} + \frac{3\alpha_1^3}{\alpha_2 u^2 h})A(5) - 6(\frac{\alpha_1^3\alpha_2}{uh^2} - \frac{\alpha_1\alpha_3^3}{(1-u)h^2})A(6)$$
$$+ \frac{\alpha_1^3\alpha_2^3}{h^3}A(7)]\cos e^{-(fg)^{\frac{1}{2}}}\,du$$

S-P Integrals

$$\langle 1s(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|2P_x(B)\rangle = C\int_o^1 [-D_x u\cos A(1) - K_x \sin A(2)]\, e^{-(fg)^{\frac{1}{2}}}\,du$$

$$\langle 2s(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|2P_x(B)\rangle = C\int_o^1 [\frac{D_x u}{\alpha_1}\cos A(1) + (\frac{K_x}{\alpha_1}\sin - D_x\,\alpha_1\cos)A(2)$$
$$- \frac{K_x\alpha_1}{u}\sin A(3)]\, e^{-(fg)^{\frac{1}{2}}}\,du$$

$$\langle 3s(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|2P_x(B)\rangle = C\int_o^1 [3\,D_x\cos A(2) + (\frac{3K_x}{u}\sin - \frac{\alpha_1^2}{u}D_x\cos)A(3)$$
$$- \frac{K_x\alpha_1^2}{u^2}\sin A(4)]\, e^{-(fg)^{\frac{1}{2}}}\,du$$

$$\langle 4s(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|2P_x(B)\rangle = C\int_o^1 [-\frac{3D_x}{\alpha_1}\cos A(2) + (-\frac{3K_x}{u\alpha_1}\sin + \frac{6\alpha_1 D_x}{u}\cos)A(3)$$
$$+ (\frac{6K_x\alpha_1}{u^2}\sin - \frac{D_x\alpha_1^3}{u^2}\cos)A(4) - \frac{K_x\alpha_1^3}{u^3}\sin A(5)]e^{-(fg)^{\frac{1}{2}}}du$$

The corresponding 3p integrals can be obtained by a single application of equation (6) to each of the above integrals. They will not be listed here.

S-D Integrals

Only integrals of the form 1s-3d and 2s-3d will be listed. The 3s-3d and 4s-3d can be obtained by one and two applications of equation (5), respectively.

$$\langle 1s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |3d_{xy}(B)\rangle = C \int_0^1 [D_x D_y u^2 \cos A(1) + (K_x D_y u + K_y D_x u) \sin A(2) - K_x K_y \cos A(3)] e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 1s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |3d_{x^2-y^2}(B)\rangle = C \int_0^1 [(D_x^2 - D_y^2)u^2 \cos A(1) + 2u \sin (K_x D_x - K_y D_y) A(2) + (K_y^2 - K_x^2) \cos A(3)] e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 1s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |3d_{3z^2-r^2}(B)\rangle = C \int_0^1 [D_z^2 u^2 \cos A(1) + (\frac{2-u}{1-u} \cos + 2D_z K_z u \sin) A(2) - (\frac{\alpha_2^2}{3(1-u)^2} \cos + K_z^2 \cos) A(3)] e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2s(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C |3d_{xy}(B)\rangle = C \int_0^1 [-\frac{u^2}{\alpha_1} D_x D_y \cos A(1) + (\alpha_1 u D_x D_y \cos - \frac{u \sin}{\alpha_1} (K_x D_y + K_y D_x)) A(2) + (\frac{K_x K_y}{\alpha_1} \cos + \alpha_1 \sin (K_x D_y + K_y D_x)) A(3) - \frac{K_x K_y}{u} \alpha_1 \cos A(4)] e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2s(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|3d_{x^2-y^2}(B)\rangle = C\int_o^1 [\frac{(D_y^2-D_x^2)}{\alpha_1} u^2 \cos A(1) + ((D_yK_y - D_xK_x)\frac{2u}{\alpha_1}\sin + \alpha_1 u \cos (D_x^2-D_y^2))A(2) + (\frac{K_x^2-K_y^2}{\alpha_1}\cos + 2\alpha_1 \sin (K_xD_x - K_yD_y))A(3) + \frac{K_y^2-K_x^2}{u}\alpha_1 \cos A(4)]$$
$$e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2s(a)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|3d_{3z^2-r^2}(B)\rangle = C\int_o^1 [-\frac{D_z^2u^2\cos}{\alpha_1} A(1) + (\alpha_1 D_z^2 u \cos - \frac{(2-u)\cos}{(1-u)\alpha_1} - \frac{2D_zK_zu\sin}{\alpha_1})A(2) + (\frac{\alpha_2^2\cos}{3\alpha_1(1-u)^2} + \frac{K_z^2\cos}{\alpha_1} + 2\alpha_1 D_zK_z\sin)A(3) - \frac{\alpha_2^2\alpha_1}{3h(1-u)} + \frac{\alpha_1K_z^2}{u}\cos A(4)]$$
$$e^{-(fg)^{\frac{1}{2}}} du$$

P-P Integrals

Only integrals of the form 2p-2p will be listed. Integrals between 2p and 3p functions can be found from these by a single application of either equation (5) or equation (6), and those between two 3p functions can be found by application of both equation (5) and equation (6) to those given.

$$\langle 2p_x(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|2p_x(B)\rangle = C\int_o^1 [-D_x^2 h \cos A(1) + (D_xK_x(2u-1)\sin + \cos)A(2) - K_x^2 \cos A(3)]\, e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2p_y(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|2p_x(B)\rangle = C\int_o^1 [-D_xD_yh \cos A(1) + (D_xK_yu - D_yK_x(1-u))\sin A(2) - K_xK_y \cos A(3)]\, e^{-(fg)^{\frac{1}{2}}} du$$

P-D Integrals

Only integrals of the form 2p-3d will be listed. Integrals between 3p and 3d functions can be found by a single application of equation (5) to those given.

$$\langle 2p_x(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C|3d_{xy}(B)\rangle = C \int_0^1 [D_x^2 D_y uh \cos A(1) + (- D_y u \cos + ((K_x D_y + K_y D_x)D_x h - D_x D_y K_x u^2)\sin) A(2) + (- K_y \sin + (K_x^2 D_y u + K_x K_y D_x u - D_x K_x K_y(1-u))\cos) A(3) + K_x^2 K_y \sin A(4)] e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2p_z(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C|3d_{xy}(B)\rangle = C \int_0^1 [D_x D_y D_z uh \cos A(1) + (K_x D_y D_z h + K_y D_x D_z h - D_x D_y K_z u^2)\sin A(2) + (K_x K_z D_y u + K_y K_z D_x u - K_x K_y D_z(1-u)\cos A(3) + K_x K_y K_z \sin A(4)] e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2p_x(A)|\cos \underset{\sim}{K}_\nu \cdot \underset{\sim}{r}_C|3d_{3z^2-r^2}(B)\rangle = C \int_0^1 [D_z^2 D_x uh \cos A(1) + (D_x(2-u)\cos + (2D_x D_z K_z h - D_z^2 K_x u^2)\sin) A(2) + (- \frac{K_x(2-u)}{1-u} \sin + (2D_z K_z K_x u - \frac{D_x \alpha_2^2}{3(1-u)} - D_x K_z^2(1-u))\cos) A(3) + (\frac{K_x \alpha_2^2}{3(1-u)^2} + K_x K_z^2) \sin A(4)] e^{-(fg)^{\frac{1}{2}}} du$$

$$\langle 2p_z(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|3d_{3z^2-r^2}(B)\rangle = C\int_0^1 [D_z{}^3uh\cos A(1) + (D_z(2-3u)\cos$$

$$+ D_z{}^2K_zu(2-3u)\sin) A(2) + (\frac{-4+3u}{1-u}K_z\sin + (K_z{}^2(3u-1)$$

$$- \frac{\alpha_2{}^2}{3(1-u)}D_z\cos) A(3) + (\frac{K_z\alpha^2}{3(1-u)^2} + K_z{}^3)\sin A(4)]$$

$$e^{-(fg)^{\frac{1}{2}}}du$$

$$\langle 2p_x(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|3d_{x^2-y^2}(B)\rangle = C\int_0^1 [(D_x{}^2-D_y{}^2)D_xuh\cos A(1)$$

$$+ (2h(K_xD_x{}^2 - K_yD_xD_y)\sin + u^2(D_y{}^2-D_x{}^2)K_x\sin$$

$$-2u\,D_x\cos) A(2) + (-2K_x\sin + (1-u)(K_y{}^2-K_x{}^2)D_x\cos$$

$$-2u\,K_x\cos(K_yD_y-K_xD_x)) A(3) + K_x(K_x{}^2-K_y{}^2)\sin A(4)]$$

$$e^{-(fg)^{\frac{1}{2}}}du$$

$$\langle 2p_z(A)|\cos \underset{\sim}{K_\nu}\cdot\underset{\sim}{r_C}|3d_{x^2-y^2}(B)\rangle = C\int_0^1 [(D_x{}^2-D_y{}^2)D_zuh\cos A(1) + 2hD_z$$

$$(K_xD_x-K_yD_y) + u^2K_z(D_y{}^2-D_x)^2)\sin A(2) + ((1-u)D_z$$

$$(K_y{}^2-K_x{}^2) + 2uK_z(K_xD_x-K_yD_y)) A(3)\cos + K_z(K_x{}^2-K_y{}^2)$$

$$\sin A(4)]e^{-(fg)^{\frac{1}{2}}}du$$

APPENDIX B

In this appendix our purpose is to describe the operations of the cubic group and to give the transformation properties of the d functions under them. Although the transformation matrix for the d functions is five by five, it can be broken down into a two by two block and a three by three block which never mix. These two blocks are treated separately.

In the tabulation below, the notation for the operations is that of Slater (1965). Only 24 of the 48 operations of the cubic group are given. The others can be found by applying the inversion operator to those shown. The d functions are invariant under the inversion operator. Each operation is identified by showing its effect on an arbitrary function of x,y,z. Then its effect on the two sets of d functions is given. Matrices are denoted by brackets rather than parentheses.

Operation	Effect on d functions
$R_1 f(x,y,z) = f(x,y,z)$	$R_1 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$
	$R_1 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$
$R_2 f(x,y,z) = f(x,-y,-z)$	$R_2 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$

$$R_2 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_3 f(x,y,z) = f(-x,y,-z)$

$$R_3 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_3 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_4 f(x,y,z) = f(-x,-y,z)$

$$R_4 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_4 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_5 f(x,y,z) = f(y,z,x)$

$$R_5 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2} \begin{vmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_5 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_6 f(x,y,z) = f(-y,z,-x)$

$$R_6 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2} \begin{vmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_6 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_7 f(x,y,z) = f(-y,-z,x)$

$$R_7 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2} \begin{vmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_7 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_8 f(x,y,z) = f(y,-z,-x)$

$$R_8 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2} \begin{vmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_8 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_9 f(x,y,z) = f(z,x,y)$

$$R_9 \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2} \begin{vmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_9 \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_{10} f(x,y,z) = f(-z,-x,y)$

$$R_{10} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2} \begin{vmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{10} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{11}f(x,y,z) = f(z,-x,-y) \qquad R_{11}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{11}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{12}f(x,y,z) = f(-z,x,-y) \qquad R_{12}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{12}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{13}f(x,y,z) = f(-x,z,-y) \qquad R_{13}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & -\sqrt{3} \\ -\sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{13}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{14}f(x,y,z) = f(-x,-z,y) \qquad R_{14}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & -\sqrt{3} \\ -\sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{14}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{15}f(x,y,z) = f(-z,-y,x) \qquad R_{15}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{15}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{16}f(x,y,z) = f(z,-y,-x) \qquad R_{16}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{16}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{17}f(x,y,z) = f(y,-x,-z) \qquad R_{17}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{17}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{18}f(x,y,z) = f(-y,x,-z) \qquad R_{18}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{18}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_{19}f(x,y,z) = f(x,z,y)$

$$R_{19}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & -\sqrt{3} \\ -\sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{19}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_{20}f(x,y,z) = f(x,-z,-y)$

$$R_{20}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & -\sqrt{3} \\ -\sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{20}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_{21}f(x,y,z) = f(z,y,x)$

$$R_{21}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{21}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$R_{22}f(x,y,z) = f(-z,y,-x)$

$$R_{22}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \frac{1}{2}\begin{vmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{vmatrix}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{22}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{vmatrix}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{23}f(x,y,z) = f(y,x,z) \qquad R_{23}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{23}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

$$R_{24}f(x,y,z) = f(-y,-x,z) \qquad R_{24}\begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix} \begin{vmatrix} 3z^2-r^2 \\ x^2-y^2 \end{vmatrix}$$

$$R_{24}\begin{vmatrix} xy \\ xz \\ yz \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{vmatrix} \begin{vmatrix} xy \\ xz \\ yz \end{vmatrix}$$

APPENDIX C

In this Appendix we have included listings of computer programs to evaluate kinetic energy, potential energy (three-center) and overlap integrals of the type ss or dd on vanadium. The programs are similar, the principle difference being in Subroutine D3INT. Subroutines which are identical in both programs are not shown and the Gaussian coefficients, V(I) and W(I), have been deleted from the second listing to conserve space. Comment cards in the listing describe the programs, and differences between ss and dd programs illustrate how other programs such as sp or sd may be constructed. These programs are not included, but can be built around the basic ss and dd programs using formulas given in Appendix A.

```
C                                                                       000
C     * * * * * * * * * * * MAIN PROGRAM VANDD * * * * * * * * * * * * OC1
C                                                                       002
      IMPLICIT REAL*8(A-F,H,O-Z)                                        003
      DIMENSION EK(15)                                                  004
      DIMENSION INDA(125),AFUN(4455),QL(5),VCL(5)                       005
      DIMENSION RK(500),B(50C),C(500),D(500),IOU(50C),ALD(5),CC(5),VK(   CC6
     1500)                                                              007
      DIMENSION SS(15)                                                  OC8
      DIMENSION SUM(20),SUM1(20)                                        009
      DIMENSION GER(40)                                                 010
      DIMENSION SOLD(20) ,SOL1(20)                                      011
      DIMENSION S  (20)                                                 012
      DIMENSION FU(1440),A(9),W(96),V(96)                               013
      COMMON/CFUN/XXX(30C),OD/FACL/BF(100)/BIGO/CON73,CON74,CON75,CON76,  014
     1CON82,CON83,CON84,CON85,CON86,CON87,CON88,CON89,W,V,S,CON77,CON78,  015
     2CON80,CON79,                                                      016
     3CON81, CON1,CON2,CON3,CON4,CON5,CON6,CON7,CON8,CON9,CON10,CON11,  C17
     1CON12,CON13,CON14,CON15,CON16,CON17,CON18,CON19,CON20,CON21,CON22,  018
     2CON23,CON24,CON25,CON26,CON27,CON28,CON29,CON30,CON31,CON32,CON33,  019
     3CON34,CON35,CON36,CON37,CON38,CON39,CON40,CON41,CON42,CON43,CON44,  C20
     4CON45,CON46,CON47,CON48,CON49,CON50,CON51,CON52,CON53,CON54,CON55,  021
     5CON56,CON57,CON58,CON59,CON60,CON61,CON62,CON63,CON64,CON65,CON66,  022
     6CON67,CON68,CON69,CON70,CON71,CON72,U,A,RAB,ALPHA1,ALPHA2,RS,FU,   023
     7AI,AJ,AK,AX,AY,AZ,BX,BY,BZ,CX,CY,CZ,AA,N                          024
C                                                                       025
C     THIS PROGRAM COMPUTES POTENTIAL,EXCHANGE,OVERLAP,AND KINETIC ENERG  026
C     INTEGRALS BETWEEN FUNCTIONS OF D SYMMETRY                         027
C                                                                       028
      V(1)= 0.016276744849602969579                                     029
      V(2)=-0.016276744849602969579                                     030
      V(3)= 0.048812985136049731112                                     031
      V(4)=-0.048812985136049731112                                     032
      V(5)= 0.081297495464425558994                                     033
      V(6)=-0.081297495464425558994                                     034
```

```
V(7)= 0.113695850110665920911                                   035
V(8)=-0.113695850110665920911                                   036
V(9)= 0.145973714654896541989                                   037
V(10)=-.145973714654896941989                                   038
V(11)=0.178096882367618602759                                   039
V(12)=-.178096882367618602759                                   040
V(13)=0.210031310460567203603                                   041
V(14)=-.210031310460567203603                                   042
V(15)=.241743156163840012328                                    043
V(16)=-.241743156163840012328                                   044
V(17)=0.273198812591049141487                                   045
V(18)=-.273198812591049141487                                   046
V(19)=0.304364944354496353024                                   047
V(20)=-.304364944354496353024                                   048
V(21)=0.335208522892625422616                                   049
V(22)=-.335208522892625422616                                   050
V(23)=0.365696861472313635031                                   051
V(24)=-.365696861472313635031                                   052
V(25)=0.395797649828908603285                                   053
V(26)=-.395797649828908603285                                   054
V(27)=0.425478988407300545365                                   055
V(28)=-.425478988407300545365                                   056
V(29)=0.454709422167743008636                                   057
V(30)=-.454709422167743008636                                   058
V(31)=0.483457973920596359768                                   059
V(32)=-.483457973920596359768                                   060
V(33)=0.511694177154667673586                                   061
V(34)=-.511694177154667673586                                   062
V(35)=0.539388108324357436227                                   063
V(36)=-.539388108324357436227                                   064
V(37)=0.566510418561397168404                                   065
V(38)=-.566510418561397168404                                   066
V(39)=0.593032364777572080684                                   067
V(40)=-.593032364777572080684                                   068
V(41)=0.618925840125468570386                                   069
V(42)=-.618925840125468570386                                   070
```

```
V(43)=0.64416340378496710C6798                071
V(44)=-.64416340378496710C6798                072
V(45)=0.66871831004391615395 3                073
V(46)=-.66871831C04391615395 3                074
V(47)=0.69256453664217156134 4                075
V(48)=-.69256453664217156134 4                076
V(49)=C.71567681234896762622 5                077
V(50)=-.71567681234896762622 5                078
V(51)=0.73803064374440013285 1                079
V(52)=-.73803064374440013285 1                080
V(53)=0.75960234117664749870 3                081
V(54)=-.75960234117664749870 3                082
V(55)=C.78036904386743321760 4                083
V(56)=-.78036904386743321760 4                084
V(57)=C.80030874413914081722 9                085
V(58)=-.80030874413914081722 9                086
V(59)=0.81940031073793167553 9                087
V(60)=-.81940031073793167553 9                088
V(61)=0.83762351122818712149 4                C89
V(62)=-.83762351122818712149 4                090
V(63)= 0.85495903343460145546 3               091
V(64)=-0.85495903343460145546 3               092
V(65)= 0.87138850590296502874                 093
V(66)=-0.87138850590296502874                 094
V(67)= 0.88689451740242041605 7               095
V(68)=-0.88689451740242041605 7               096
V(69)= 0.90146063531585234131 9               097
V(70)=-0.90146063531585234131 9               098
V(71)= 0.91507142312089807420 6               099
V(72)=-0.91507142312089807420 6               100
V(73)= 0.92771245672230869096 5               101
V(74)=-0.92771245672230869096 5               102
V(75)= 0.93937033975275521693 2               103
V(76)=-0.93937033975275521693 2               104
V(77)= 0.95003271778443763575 6               105
V(78)=-0.95003271778443763575 6               106
```

```
V(79)= 0.95968829144874253 93                                    107
V(80)=-0.95968329144874253 93                                    108
V(81)= 0.96832632946326421217 4                                  109
V(82)=-0.96832682946326421217 4                                  110
V(83)= 0.97593917458513646645 3                                  111
V(84)=-0.97593917458513646645 3                                  112
V(85)= 0.98251726356301467744 7                                  113
V(86)=-0.98251726356301467744 7                                  114
V(87)= 0.98805412632962379948 1                                  115
V(88)=-0.98805412632962379948 1                                  116
V(89)= 0.99254390032376262457 2                                  117
V(90)=-0.99254390032376262457 2                                  118
V(91)= 0.99598184298720929065 0                                  119
V(92)=-0.99598184298720929065 0                                  120
V(93)= 0.99836437586318167772 4                                  121
V(94)=-0.99836437586318167772 4                                  122
V(95)= 0.99968950388323076682 8                                  123
V(96)=-0.99968950388323076682 8                                  124
W(1)=0.032550614492363166242                                     125
W(2)=0.032550614492363166242                                     126
W(3)=0.032516118713868835987                                     127
W(4)=0.032516118713868835987                                     128
W(5)=0.032447163714064269364                                     129
W(6)=0.032447163714064269364                                     130
W(7)=0.032343822568575928429                                     131
W(8)=0.032343822568575928429                                     132
W( 9)=0.032206204794030250669                                    133
W(10)=0.032206204794030250669                                    134
W(11)=0.032034456231992663218                                    135
W(12)=0.032034456231992663218                                    136
W(13)=0.031828752894411006535                                    137
W(14)=0.031828752894411006535                                    138
W(15)=0.031589330770727168558                                    139
W(16)=0.031589330770727168558                                    140
W(17)=0.031316425596861355813                                    141
W(18)=0.031316425596861355813                                    142
```

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W(19)=0.031010332586313837423                                    143
W(20)=0.031010332586313837423                                    144
W(21)=0.030671376123669149014                                    145
W(22)=0.030671376123669149014                                    146
W(23)=0.030299915420827593794                                    147
W(24)=0.030299915420827593794                                    148
W(25)=0.029896344136328385984                                    149
W(26)=0.029896344136328385984                                    150
W(27)=0.029461089958167905970                                    151
W(28)=0.029461089958167905970                                    152
W(29)=0.028994614150555236543                                    153
W(30)=0.028994614150555236543                                    154
W(31)=0.028497411065085385646                                    155
W(32)=0.028497411065085385646                                    156
W(33)=0.027970007616848334440                                    157
W(34)=0.027970007616848334440                                    158
W(35)=0.027412962726029242823                                    159
W(36)=0.027412962726029242823                                    160
W(37)=0.026826866725591762198                                    161
W(38)=0.026826866725591762198                                    162
W(39)=0.026212340735672413913                                    163
W(40)=0.026212340735672413913                                    164
W(41)=0.025570036005349361499                                    165
W(42)=0.025570036005349361499                                    166
W(43)=0.024900633222483610288                                    167
W(44)=0.024900633222483610288                                    168
W(45)=0.024204841792364691282                                    169
W(46)=0.024204841792364691282                                    170
W(47)=0.023483399585926219842                                    171
W(48)=0.023483399585926219842                                    172
W(49)=0.022737069658329374001                                    173
W(50)=0.022737069658329374001                                    174
W(51)=0.021966644438744349195                                    175
W(52)=0.021966644438744349195                                    176
W(53)=0.021172939892191298988                                    177
W(54)=0.021172939892191298988                                    178
```

```
W(55)=0.020356797154333324595                                    179
W(56)=0.020356797154333324595                                    180
W(57)=0.019519081140145022410                                    181
W(58)=0.019519081140145022410                                    182
W(59)=0.018660679627411467385                                    183
W(60)=0.018660679627411467385                                    184
W(61)=0.017782502316045260838                                    185
W(62)=0.017782502316045260838                                    186
W(63)=0.016885479864245172450                                    187
W(64)=0.016885479864245172450                                    188
W(65)=0.015970562902562291381                                    189
W(66)=0.015970562902562291381                                    190
W(67)=0.015038721026994938006                                    191
W(68)=0.015038721026994938006                                    192
W(69)=0.014090941772314860916                                    193
W(70)=0.014090941772314860916                                    194
W(71)=0.013128229566961572637                                    195
W(72)=0.013128229566961572637                                    196
W(73)=0.012151604671088319635                                    197
W(74)=0.012151604671088319635                                    198
W(75)=0.011162102099838498591                                    199
W(76)=0.011162102099838498591                                    200
W(77)=0.010160770535008415758                                    201
W(78)=0.010160770535008415758                                    202
W(79)=0.009148671230783386633                                    203
W(80)=0.009148671230783386633                                    204
W(81)=0.008126876925698759217                                    205
W(82)=0.008126876925698759217                                    206
W(83)=0.007096470791153865269                                    207
W(84)=0.007096470791153865269                                    208
W(85)=0.006058545504235961683                                    209
W(86)=0.006058545504235961683                                    210
W(87)=0.005014202742927517693                                    211
W(88)=0.005014202742927517693                                    212
W(89)=0.003964554338444686674                                    213
W(90)=0.003964554338444686674                                    214
```

```
      W(91)=0.C0291073181793494640B                                      215
      W(92)=0.C0291073181793494640B                                      216
      W(93)=0.00185396C738946921732                                      217
      W(94)=0.C0185396C738946921732                                      218
      W(95)=C.0007967920655520C2429                                      219
      W(96)=C.0007967920655520C2429                                      220
C     READ OR WRITE THE FILE IDENTIFICATION ON THE TAPE                  221
C     WRITE(3,16)                                                        222
C  16 FORMAT(1X,'O-O INTEGRALS V-V')                                     223
      READ(3,16)(GER(N),N=1,6)                                           224
   16 FORMAT(6A3)                                                        225
      READ(5,6)(GER(I),I=1,30)                                           226
    6 FORMAT(26A3/4A3)                                                   227
C     READ NUMBER OF TERMS TO BE INCLUDED IN FOURIER SERIES              228
      READ(5,101)JJJJ                                                    229
  101 FORMAT(I5)                                                         230
C     PARAMETER KKR                                                      231
C       1 COMPUTES EXCHANGE ONLY                                         232
C       2 COMPUTES POTENTIAL ONLY                                        233
C       3 COMPUTES POTENTIAL AND EXCHANGE                                234
      READ(5,101)KKR                                                     235
C     READ A/2                                                           236
      READ(5,641)QA                                                      237
  641 FORMAT(F9.6)                                                       238
      GOTO (17,11,11),KKR                                                239
C     READ FOURIER COEFFICIENTS OF POTENTIAL                             240
C    SUM ONLY OVER VECTORS HAVING NON-NEGATIVE COMPONENTS.PARAMETER IOU   241
C     DENOTES THE NUMBER OF ZERO COMPONENTS IN EACH VECTOR               242
   11 DO 400 J=1,JJJJ                                                    243
  400 READ(5,5)VK(J),B(J),C(J),D(J),IOU(J)                               244
    5 FORMAT(1XD16.8,3F6.2,I5)                                           245
      IF(KKR.EQ.2)GOTO 402                                               246
C     READ FOURIER COEFFICIENTS OF EXCHANGE                              247
   17 DO401 J=1,JJJJ                                                     248
  401 READ(5,5)RK(J)      ,B(J),C(J),D(J),IOU(J)                         249
  402 CONTINUE                                                           250
```

```
C      READ D WAVEFUNCTIONS FOR VANADIUM IN FOLLOWING ORDER                    251
C EXPON  COEFF                                                                 252
C 3.0248 5.16807                                                               253
C 9.971 38.69851                                                               254
C 4.792 31.22514                                                               255
C 2.0756 2.39639                                                               256
C 1.172  0.09345                                                               257
       DO10 J=1,5                                                              258
   10 READ(5,3)ALD(J),CD(J)                                                    259
    3 FORMAT(2F8.5)                                                            260
C      READ DIRECT LATTICE COORDINATES                                         261
   60 READ(5,4)AX,AY,AZ,BX,BY,BZ,CX,CY,CZ                                     262
    4 FORMAT(9F8.5)                                                            263
       DO398J=1,15                                                             264
       SS(J)=0.DO                                                              265
       SOLI(J)=0.0                                                             266
  398 SOLD(J)=0.DO                                                             267
       CON1=BX-AX                                                              268
       CON2=BY-AY                                                              269
       CON3=BZ-AZ                                                              270
       CON4=CON1**2                                                            271
       CON5=CON2**2                                                            272
       CON6=CON3**2                                                            273
       CON7=CON1**3                                                            274
       CON8=CON2**3                                                            275
       CON9=CON3**3                                                            276
       CON10=CON1*CON2                                                         277
       CON11=CON2*CON3                                                         278
       CON12=CON1*CON3                                                         279
       CON13=CON4+CON5                                                         280
       CON14=CON4+CON6                                                         281
       CON15=CON5+CON6                                                         282
       CON16=CON4*CON5                                                         283
       CON17=CON4*CON6                                                         284
       CON18=CON5*CON6                                                         285
       CON19=CON4*CON2                                                         286
```

```
      CON20=CON4*CON3                                                   287
      CON21=CON5*CON1                                                   288
      CON22=CON5*CON3                                                   289
      CON23=CON6*CON1                                                   290
      CON24=CON6*CON2                                                   291
      CON25=CON10*CON3                                                  292
      CON26=CON19*CON3                                                  293
      CON27=CON21*CON3                                                  294
      CON29=CON23*CON2                                                  295
      CON34=CON4-CON5                                                   296
      IF(DABS(CON34).GT.0.00001)GO TO 26                                297
      CON34=0.D0                                                        298
   26 CON30=CON34**2                                                    299
      CON29=CON34*CON10                                                 300
      CON80=CON34*CON11                                                 301
      CON31=CON8*CON3                                                   302
      CON32=CON9*CON2                                                   303
      CON33=CON9*CON1                                                   304
C     SUM OVER DIFFERENT PAIRS OF TERMS IN THE WAVEFUNCTIONS            305
      DO40L=1,5                                                         306
      DO 40 K=1,L                                                       307
      IF(L.EQ.K)GO TO 30                                                308
      COC=2.0*CO(L)*CO(K)                                               309
      GO TO 50                                                          310
   30 COC=CO(L)*CO(K)                                                   311
   50 ALPHA1=ALO(L)                                                     312
      ALPHA2=ALO(K)                                                     313
      CON35=ALPHA1*ALPHA1/3.0                                           314
      CON36=ALPHA2*ALPHA2/3.0                                           315
      CON37=CON9*CON3                                                   316
      CON38=ALPHA1*ALPHA1                                               317
      CON39=ALPHA2*ALPHA2                                               318
      CON40=CON38*CON39                                                 319
      CON41=CON40*ALPHA1                                                320
      CON42=CON38*ALPHA1                                                321
      CON43=CON39*ALPHA1                                                322
```

```
CON44=CON40*ALPHA2                                                    323
CON45=CON42*ALPHA2                                                    324
CON46=CON39*ALPHA2                                                    325
CON47=CON46*ALPHA1                                                    326
CON48=ALPHA1*ALPHA2                                                   327
CON49=CON46/ALPHA1                                                    328
CON50=CON42/ALPHA2                                                    329
CON51=ALPHA1/ALPHA2                                                   330
CON52=ALPHA2/ALPHA1                                                   331
CON53=1.0/ALPHA1                                                      332
CON54=1.0/ALPHA2                                                      333
CON55=1.0/CON48                                                       334
CON56=CON39*CON53                                                     335
CON57=CON51*ALPHA1                                                    336
CON58=CON48*ALPHA1                                                    337
CON59=ALPHA1*CON4                                                     338
CON60=ALPHA1*CON2                                                     339
CON61=CON2*CON60                                                      340
CON62=ALPHA1*CON1                                                     341
CON63=CON2/ALPHA1                                                     342
CON64=CON3/ALPHA1                                                     343
CON65=CON3*ALPHA1                                                     344
CON66=CON65*CON3                                                      345
CON67=CON53*CON25                                                     346
CON68=CON25*ALPHA1                                                    347
CON69=CON34*CON1                                                      348
CON70=CON34*CON2                                                      349
CON71=CON53*CON23                                                     350
CON72=CON53*CON24                                                     351
CON73=CON36*CON10                                                     352
CON74=CON36*CON11                                                     353
CON75=CON36*CON12                                                     354
CON76=(CON35+CON36)*CON6                                              355
CON77=CON3*CON36                                                      356
CON78=CON3*CON35                                                      357
CON79=CON35*CON36                                                     358
```

```
      CON81=CON12*CON34                                                  359
      CON82=CON19*CON53                                                  360
      CON83=CON53*CON10                                                  361
      CON84=CON53*CON4                                                   362
      CON85=ALPHA1*CON10                                                 363
      CON86=ALPHA1*CON4                                                  364
      CON87=CON21*CON53                                                  365
      CON88=CON5*CON53                                                   366
      CON89=CON48*CON6                                                   367
      RAB=DSQRT(CON1**2+CON2**2+CON3**2)                                 368
      AA=2.*3.14159*ALPHA1*ALPHA2*RAB**3                                 369
      DO100N=1,15                                                        370
      SUM1(N)=0.0                                                        371
  100 SUM(N)=0.DO                                                        372
C     SUM THE FOURIER SERIES                                             373
      DO500 J=1,JJJJ                                                     374
      DO80KOL=1,1440                                                     375
   80 FU(KOL)=0.DO                                                       376
      N=IOU(J)                                                           377
      AI=3.14159265/QA*B(J)                                              378
      AJ=3.14159265/QA*C(J)                                              379
      AK=3.14159265/QA*D(J)                                              380
      SK    =DSQRT(AI*AI+AJ*AJ+AK*AK)                                    381
      RS=SK*SK                                                           382
C                                                                        383
C     SUBROUTINES D3INT,AGET,AND INTEG COMPUTE THE THREE-CENTER INTEGRAL 384
C     IF THE INTEGRALS HAVE BEEN STORED ON TAPE,READ THE TAPE INSTEAD OF 385
C     CALLING D3INT                                                      386
C                                                                        387
C     CALL D3INT                                                         388
C     WRITE(3)(S(N),N=1,15)                                              389
      READ(3)(S(N),N=1,15)                                               390
      DO146N=1,15                                                        391
      IF(J.NE.1)GOTO145                                                  392
      SS(N)=SS(N)+S(N)*COC                                               393
  145 GOTO (147,148,148),KKR                                             394
```

```
      STOP                                                              395
  148 SUM1(N)=SUM1(N)+RK(J)*S(N)                                        396
      IF(KKR.EQ.2)GOTO 146                                              397
  147 SUM(N)=SUM(N)+VK(J)*S(N)                                          398
  146 CONTINUE                                                          399
  500 CONTINUE                                                          400
      DO408J=1,15                                                       401
      SOL1(J)=SUM1(J)*CDC+SOL1(J)                                       402
  408 SOLD(J)=SUM(J)*CDC+SOLD(J)                                        403
   40 CONTINUE                                                          404
      WRITE(6,2)AX,AY,AZ                                                405
      WRITE(6,2)BX,BY,BZ                                                406
      WRITE(6,2)CX,CY,CZ                                                407
    2 FORMAT(1X,3F10.6)                                                 408
C                                                                       409
C     COMPUTE KINETIC ENERGY INTEGRALS                                  410
C     SEE SUBROUTINE SZE FOR DESCRIPTION OF THE PARAMETERS              411
C                                                                       412
      NA=3                                                              413
      NB=3                                                              414
      LA=2                                                              415
      LB=2                                                              416
      CA=28.                                                            417
      CB=28.                                                            418
      VOL(1)=1.D0/6.D0                                                  419
      VOL(2)=2.D0/3.D0                                                  420
      VOL(3)=1.D0                                                       421
      VOL(4)=VOL(2)                                                     422
      VOL(5)=VOL(1)                                                     423
      CALL FACGEN(BF)                                                   424
      CALL AGENT(INDA,AFUN)                                             425
      DD=RAB                                                            426
      DDP=0.0                                                           427
      DDD=0.0                                                           428
      DDS=0.0                                                           429
      DO 200 J=1,5                                                      430
```

```
      DO 200 K=1,5                                                          431
      XA=ALD(J)                                                             432
      XB=ALD(K)                                                             433
      COJ=5.6250/((ALD(J)**3.5)*(ALD(K)**3.5))                              434
      DO 300 L=1,5                                                          435
      MA=L-3                                                                436
      MB=MA                                                                 437
      ABK=VOL(L)                                                            438
      CALL SZE(E,ZA,ZB,NA,LA,MA,XA,CA,NB,LB,MB,XB,CB,ABK,INDA,AFUN)         439
  300 QL(L)=E                                                               440
C     COMPUTE PARAMETERS FOR THE TWO-CENTER INTEGRALS                       441
      DDS=DDS+QL(3)*CO(J)*CO(K)*2.0*COJ                                     442
      DDP=DDP+(QL(2)+QL(4))*CO(J)*CO(K)*COJ                                 443
  200 DDD=DDD+(QL(1)+QL(5))*CO(J)*CO(K)*COJ                                 444
      CALL NIT(EK,CON1,CON2,CON3,RAB,DDD,DDP,DDS)                           445
      N1=AX/QA+0.1                                                          446
      N2=AY/QA+0.1                                                          447
      N3=AZ/QA+0.1                                                          448
      PUNCH 108,N1,N2,N3                                                    449
  108 FORMAT(3I5)                                                           450
      DO407J=1,15                                                           451
      IF(KKR.NE.3)GOTO 28                                                   452
      PUNCH 107,SOLD(J),EK(J),SOL1(J),SS(J)                                 453
  107 FORMAT(4E16.8)                                                        454
   28 KK=2 *J-1                                                             455
      WRITE(6,8)GER(KK),GER(KK+1)                                           456
    8 FORMAT(1X,2A3)                                                        457
      WRITE(6,1)SOLD(J),EK(J),SOL1(J),SS(J)                                 458
    1 FORMAT(1X,'POTENTIAL=',E16.8,' KINETIC ENERGY=',E16.8,' EXCHANGE='    459
     1,E16.8,' OVERLAP=',E16.8)                                             460
      WRITE(6,974)                                                          461
  974 FORMAT(1X,1H )                                                        462
  407 CONTINUE                                                              463
      GO TO 60                                                              464
      END                                                                   465
```

```
      SUBROUTINE AGET (EAX)                                                 000
      IMPLICIT REAL*8(A-H,O-Z)                                              001
      DIMENSION S  (20)                                                     002
      DIMENSION FU(1440),A(9),W(96),V(96)                                   003
      COMMON/BIGD/CON73,CON74,CON75,CON76,CON82,CON83,CON84,CON85,CON86,     004
     1CON87,CON88,CON89,W,V,S,CON77,CON78,CON80,CON79,                      005
     3CON81, CON1,CON2,CON3,CON4,CON5,CON6,CON7,CON8,CON9,CON10,CON11,      006
     1CON12,CON13,CON14,CON15,CON16,CON17,CON18,CON19,CON20,CON21,CON22,     007
     2CON23,CON24,CON25,CON26,CON27,CON28,CON29,CON30,CON31,CON32,CON33,     008
     3CON34,CON35,CON36,CON37,CON38,CON39,CON40,CON41,CON42,CON43,CON44,     009
     4CON45,CON46,CON47,CON48,CON49,CON50,CON51,CON52,CON53,CON54,CON55,     010
     5CON56,CON57,CON58,CON59,CON60,CON61,CON62,CON63,CON64,CON65,CON66,     011
     6CON67,CON68,CON69,CON70,CON71,CON72,U,A,RAB,ALPHA1,ALPHA2,RS,FU,       012
     7A1,AJ,AK,AX,AY,AZ,BX,BY,BZ,CX,CY,CZ,AA,N                              013
      F=U*(1.-U)*RAB**2                                                     014
      G=RS+ALPHA2**2/(1.-U)+ALPHA1**2/U                                     015
      FG=F*G                                                                016
      DOB=DSQRT(FG)                                                         017
      D1=DOB**3                                                             018
      D2=DOB*D1                                                             019
      D3=D2*DOB                                                             020
      D4=D1*D1                                                              021
      D5=D1*D2                                                              022
      D6=D2*D2                                                              023
      D7=D1*D4                                                              024
      D8=D3*D3                                                              025
      D9=D1*D6                                                              026
      D10=D4*D4                                                             027
      D11=D4*D5                                                             028
      A(1)=F*(3./D3+3./D2+1./D1)                                            029
      A(2)=F*F*(15./D5+15./D4+6./D3+1./D2)                                  030
      A(3)=F**3*(105./D7+105./D6+45./D5+10./D4+1./D3)                       031
      A(4)=F**4*(945./D9+945./D8+420./D7+105./D6+15./D5+1./D4)              032
      A(5)=F**5*(10395./D11+10395./D10+4725./D9+1260./D8+210./D7+21./D6     033
     1+1./D5)                                                               034
```

```
      A(6)=F**2*(105./D7+105./D6+45./D5+10./D4+1./D3)*RAB**2                    035
      A(7)=F**2*(945./D9+945./D8+420./D7+105./D6+15./D5+1./D4)*RAB**4           036
      A(8)=F**3*(10395./D11+10395./D10+4725./D9+1260./D8+210./D7+21./D6         037
     1+1./D5)*RAB**4                                                            038
      IF(DOB.GT.40.)GOTO 222                                                    039
      EAX=DEXP(-DOB)                                                            040
      GOTO 223                                                                  041
  222 EAX=0.0                                                                   042
  223 RETURN                                                                    043
      END                                                                       044
```

```
      SUBROUTINE INTEG                                                      000
      IMPLICIT REAL*8(A-H,O-Z)                                              001
      DIMENSION S  (20)                                                     002
      DIMENSION FU(1440),A(9),W(96),V(96)                                   003
      COMMON/BIGD/CON73,CON74,CON75,CON76,CON82,CON83,CON84,CON85,CON86,     004
     1CON87,CON88,CON89,W,V,S,CON77,CON78,CON80,CON79,                      005
     3CON81, CON1,CON2,CON3,CON4,CON5,CON6,CON7,CON8,CON9,CON10,CON11,      006
     1CON12,CON13,CON14,CON15,CON16,CON17,CON18,CON19,CON20,CON21,CON22,     007
     2CON23,CON24,CON25,CON26,CON27,CON28,CON29,CON30,CON31,CON32,CON33,     008
     3CON34,CON35,CON36,CON37,CON38,CON39,CON40,CON41,CON42,CON43,CON44,     009
     4CON45,CON46,CON47,CON48,CON49,CON50,CON51,CON52,CON53,CON54,CON55,     010
     5CON56,CON57,CON58,CON59,CON60,CON61,CON62,CON63,CON64,CON65,CON66,     011
     6CON67,CON68,CON69,CON70,CON71,CON72,U,A,RAB,ALPHA1,ALPHA2,RS,FU,       012
     7AI,AJ,AK,AX,AY,AZ,BX,BY,BZ,CX,CY,CZ,AA,N                              013
      DO 49 I=1,15                                                          014
      DO 50 J=1,96                                                          015
      M=J+(I-1)*96                                                          016
50    S(I)=S(I)+W(J)*FU(M)                                                  017
49    CONTINUE                                                              018
      DO 51 I=1,15                                                          019
51    S(I)=S(I)*0.500                                                       020
      RETURN                                                                021
      END                                                                   022
```

```
      SUBROUTINE D3INT                                                  000
      IMPLICIT REAL*8(A-H,O-Z)                                          001
      DIMENSION S  (20)                                                 002
      DIMENSION FU(1440),A(9),W(96),V(96)                               003
      COMMON/BIGD/CON73,CON74,CON75,CON76,CON82,CON83,CON84,CON85,CON86,  004
     1CON87,CON88,CON89,W,V,S,CON77,CON78,CON80,CON79,                   005
     3CON91, CON1,CON2,CON3,CON4,CON5,CON6,CON7,CON8,CON9,CON10,CON11,   006
     1CON12,CON13,CON14,CON15,CON16,CON17,CON18,CON19,CON20,CON21,CON22,  007
     2CON23,CON24,CON25,CON26,CON27,CON28,CON29,CON30,CON31,CON32,CON33,  008
     3CON34,CON35,CON36,CON37,CON38,CON39,CON40,CON41,CON42,CON43,CON44,  009
     4CON45,CON46,CON47,CON48,CON49,CON50,CON51,CON52,CON53,CON54,CON55,  010
     5CON56,CON57,CON58,CON59,CON60,CON61,CON62,CON63,CON64,CON65,CON66,  011
     6CON67,CON68,CON69,CON70,CON71,CON72,U,A,RAB,ALPHA1,ALPHA2,RS,FU,   012
     7AI,AJ,AK,AX,AY,AZ,BX,BY,BZ,CX,CY,CZ,AA,N                          013
      DO150J=1,15                                                       014
150   S(J)=0.0                                                          015
      ACON1=AI*AI                                                       016
      ACON2=AJ*AJ                                                       017
      ACON3=AK*AK                                                       018
      ACON4=ACON1*AI                                                    019
      ACON5=ACON2*AJ                                                    020
      ACON6=ACON3*AK                                                    021
      ACON7=ACON6*AK                                                    022
      ACON8=AI*AJ                                                       023
      ACON9=AI*AK                                                       024
      ACON10=AK*AJ                                                      025
      ACON11=ACON1*AJ                                                   026
      ACON12=ACON1*AK                                                   027
      ACON13=ACON2*AI                                                   028
      ACON14=ACON2*AK                                                   029
      ACON15=ACON3*AI                                                   030
      ACON16=ACON3*AJ                                                   031
      ACON17=ACON1*ACON2                                                032
      ACON18=ACON1*ACON3                                                033
      ACON19=ACON2*ACON3                                                034
```

```
      ACON20=AI*AJ*AK                                                   035
      ACON21=ACON1+ACON2                                                036
      ACON22=ACON1+ACON3                                                037
      ACON23=ACON2+ACON3                                                038
      ACON24=ACON13*AK                                                  039
      ACON25=ACON16*AI                                                  040
      ACON26=ACON11*AK                                                  041
      ACON27=ACON1-ACON2                                                042
      IF(DABS(ACON27).GT.0.00001)GO TO 38                               043
      ACON27=0.D0                                                       044
   38 ACON28=ACON27**2                                                  045
      ACON29=ACON6*AI                                                   046
      ACON30=ACON6*AJ                                                   047
      ACON31=ACON8*ACON27                                               048
      ACON32=ACON27*ACON10                                              049
      ACON34=ACON27*ACON9                                               050
      ACON33=-ACON34                                                    051
      GOTO(10,11,12,15),N                                               052
   15 CON=1.D0                                                          053
      GOTO 206                                                          054
   10 CON=8.D0                                                          055
      GOTO 206                                                          056
   11 CON=4.D0                                                          057
      GOTO 206                                                          058
   12 CON=2.D0                                                          059
C     SUM OVER THE 96 POINTS IN THE GAUSSIAN INTEGRATION FORMULA        060
  206 DO 750 J=1,96                                                     061
      U=(V(J)+1.D0)*0.5D0                                               062
      DX=AX*U+BX*(1.-U)                                                 063
      DY=AY*U+BY*(1.-U)                                                 064
      DZ=AZ*U+BZ*(1.-U)                                                 065
      RCDX=DX-CX                                                        066
      RCDY=DY-CY                                                        067
      RCDZ=DZ-CZ                                                        068
      S1=DSIN(AI*RCDX)                                                  069
      S2=DSIN(AJ*RCDY)                                                  070
```

```
S3=DSIN(AK*RCDZ)                                                    071
C1=DCOS(AI*RCDX)                                                    072
C2=DCOS(AJ*RCDY)                                                    073
C3=DCOS(AK*RCDZ)                                                    074
SA=S1*C2*C3*CON                                                     075
SB=C1*S2*C3*CON                                                     076
SC=C1*C2*S3*CON                                                     077
SD=-S1*S2*S3*CON                                                    078
CD=C1*C2*C3*CON                                                     079
CC=-S1*S2*C3*CON                                                    080
CB=-S1*C2*S3*CON                                                    081
CA=-C1*S2*S3*CON                                                    082
CAB=1.0-U                                                           083
HH=U*(1.0-U)                                                        084
HHH=HH*HH                                                           085
CER=1.-3.*U                                                         086
CIL=2.-3.*U                                                         087
CUB=-4.+3.*U                                                        088
COR=2.0*U-1.0                                                       089
CAB2=U*U                                                            090
CAB3=CAB*CAB                                                        091
CAB4=U*HH                                                           092
CAB5=CAB*HH                                                         093
CAB6=HHH*U                                                          094
CAB7=CAB2*HH                                                        095
CAB8=CAB3*HH                                                        096
CAB9=CAB2*U                                                         097
CAB10=CAB3*CAB                                                      098
CAB11=2.-U                                                          099
CAB12=CAB11/CAB                                                     100
CAB13=CAB11/HH                                                      101
CAB14=CAB11/CAB4                                                    102
CAB15=CAB14/U                                                       103
CAB16=U/CAB                                                         104
CAB17=COR*U                                                         105
CAB18=COR/U                                                         106
```

```
      CAB19=CAB11/U                                                          107
      CAB20=COR/CAB                                                          108
      CAB21=COR/HH                                                           109
      CAB22=CER/U                                                            110
      COR=COR*COR                                                            111
      CALL AGET(EAX)                                                         112
      IF(EAX.EQ.0.0)GOTO750                                                  113
C                                                                            114
C     FOLLOWING ARE THE EXPRESSIONS FOR THE 15 DIFFERENT D-D INTEGRALS       115
C                                                                            116
      COR78=CON37*CO                                                         117
      COR79=-2.0*CON9*AK*SC                                                  118
      COR80=CON6*CO                                                          119
      COR81=6.0*CON3*AK*SC                                                   120
      COR82= CON6*ACON3*CO                                                   121
      COR83=(3.0-CON76)*CO                                                   122
      COR84=2.0*CO                                                           123
      COR85=2.0*ACON6*CON3*SC                                                124
      COR86=2.0*AK*CON77*SC                                                  125
      COR87=-2.0*AK*CON78*SC                                                 126
      COR88=ACON3*CO                                                         127
      COR89=-2.0*CON35*CO                                                    128
      COR90=-2.0*CON36*CO                                                    129
      COR91=(CON36+CON35)*CO                                                 130
      COR92=ACON7*CO                                                         131
      COR93=ACON3*CON36*CO                                                   132
      COR94=ACON3*CON35*CO                                                   133
      COR95=CON79*CO                                                         134
      FU(J)=(COR78*HHH*A(1)+(COR*COR79*HH+(2.0-6.*HH)*COR80)*A(2)+(HH*(      135
     1COR81*COR+COR82*(6.D0*HH-1.D0)+COR83)+COR84)*A(6)+(-HHH*COR85*COR+     136
     2HH*(COR86*U+COR87*CAB)+(-1.0-6.0*HH)*HH*COR88+COR89*CAB+COR90*U        137
     3 +COR91*HH)*A(7)+(COR92*HHH+COR93*CAB2+COR94*CAB3+COR95)*A(8))*EAX     138
     4 *AA*0.89524655                                                        139
      M=J+96                                                                 140
      Q1=CON16*CO                                                            141
      B2=-CON13*CO                                                           142
```

```
      B3=AI*CON21*SA+AJ*CON19*SB                                        143
      B4=ACON8*CC*CON10                                                 144
      B5=(ACON1*CON5+CON4*ACON2)*CO                                     145
      B6=AJ*CON2*SB+AI*CON1*SA                                          146
      B7=-ACON21*CO                                                     147
      B8=ACON11*CON2*SB+ACON13*CON1*SA                                  148
      B9=ACON17*CO                                                      149
      FU(M)=(Q1*HHH*A(1)+(B2-B3*COR)*HH*A(2)+(-B4*COB+CO+B5*HH+B6*COR)*A 150
     1(3)+(B7-B8*COR)*A(4)+B9*A(5))*EAX*AA*1.19366207                   151
      M=J+192                                                           152
      W1=CON17*CO                                                       153
      W2=-CON14*CO                                                      154
      W3=AK*CON20*SC+SA*AI*CON23                                        155
      W4=ACON9*CON12*CB                                                 156
      W5=(ACON3*CON4+CON6*ACON1)*CO                                     157
      W6=AI*CON1*SA+AK*CON3*SC                                          158
      W7=-ACON22*CO                                                     159
      W8=ACON15*CON1*SA+ACON12*CON3*SC                                  160
      W9=ACON18*CO                                                      161
      FU(M)=(W1*HHH*A(1)+(W2-W3*COR)*HH*A(2)-(W4*COB-W5*HH-CO-W6*COR)*A( 162
     13)+(W7-W8*COR)*A(4)+W9*A(5))*EAX*AA *1.19366207                   163
      M=J+288                                                           164
      COR1=CON2*AJ*SB+CON3*AK*SC                                        165
      COR2=(ACON10*CON11*CA)                                            166
      COR3=(ACON2*CON6+ACON3*CON5)*CO                                   167
      COR4=CON18*CO                                                     168
      COR5=-CON15*CO                                                    169
      COR6=CON24*AJ*SB+CON22*AK*SC                                      170
      COR7=-ACON23*CO                                                   171
      COR8=ACON14*CON3*SC+ACON16*CON2*SB                                172
      COR9=ACON19*CO                                                    173
      FU(M)=((COR1*COR-COB*COR2+COR3*HH+CO)*A(3)+COR4*HHH*A(1)+(COR5-   174
     1COR6*COR)*HH*A(2)+(COR7-COR8*COR)*A(4)+COR9*A(5))*EAX*AA*1.1936620 175
     27                                                                 176
      M=J+384                                                           177
      COR38=CON30*CO                                                    178
```

```
 COR39=-4.0*CON13*CO                                                    179
 COR40=2.0*(AI*CON21*SA+AJ*CON19*SB-CON7*AI*SA-CON8*AJ*SB)              180
 COR41= (CON4*ACON1+ACON2*CON5)*CO                                      181
 COR42=(ACON2*CON4+ACON1*CON5)*CO                                       182
 COR43=-8.0*CON10*ACON8*CC                                              183
 COR44=4.0*CO                                                           184
 COR45=2.*(-CON1*ACON4*SA+ACON13*CON1*SA+(ACON11*CON2-CON2*ACON5)*      185
1SB)                                                                    186
 COR46=-4.0*ACON21*CO                                                   187
 COR47=ACON28*CO                                                        188
 COR48=4.0*(AI*CON1*SA+AJ*CON2*SB)                                      189
 FU(M)=(COR38*HHH*A(1)+(COR39+COR*COR40)*HH*A(2)+(COR*COR48+(6.0*HH     190
1-1.0)*COR41+(1.0-2.0*HH)*COR42+HH*COR43+COR44)*A(3)+(COR*COR45         191
2+COR46)*A(4)+COR47*A(5))*EAX*AA*0.29841552                             192
 M=J+480                                                                193
 COR24=CON28*CO                                                         194
 COR25=-CON10*CO                                                        195
 COR26=CON24*AI*SA                                                      196
 COR27=-CON23*AJ*SB                                                     197
 COR28=CON25*AK*SC                                                      198
 COR29=ACON9*CON11*CB+ACON3*CON10*CC+ACON8*CON6*CC+ACON10*CON12*CA      199
 COR30=-ACON9*CON11*CB                                                  200
 COR31=-ACON10*CON12*CA                                                 201
 COR32=-AI*CON2*SA                                                      202
 COR33=CON1*AJ*SB                                                       203
 COR34=ACON15*CON2*SA+ACON20*CON3*SD                                    204
 COR35=-ACON20*CON3*SD-ACON16*CON1*SB                                   205
 COR36=-ACON8*CC                                                        206
 COR37=ACON25*CC                                                        207
 FU(M)= (COR24*HHH*A(1)+(COR25+COR26*CAB+COR27*U-COR28*COR)*HH*A(2)     208
1+(HH*COR29+COR30*CAB3+COR31*CAB2+COR32*CAB+COR33*U)*A(3)+(CA8*COR     209
234+U*COR35+COR36)*A(4)+COR37*A(5))*EAX*AA*1.19366207                   210
 M=J+576                                                                211
 T1=(CON17-CON18)*CO                                                    212
 T2=2.*CON34*CO                                                         213
 T3=-CON34*CO                                                           214
```

```
 T4=AK*CON3*CON34*SC*2.0*HH                                                    215
 T5=2.*(AJ*CON24*SB-AI*CON23*SA)                                               216
 T6=-2.*(AJ*CON2*SB-AI*CON1*SA)                                                217
 T7=CON36*CON5*CO                                                              218
 T8=-ACON3*CON34*CO                                                            219
 T9=-CON6*ACON27*CO                                                            220
 T10=-CON36*CON4*CO                                                            221
 T11=4.*(ACON9*CON12*CB-ACON10*CON11*CA)                                       222
 T12=2.*(ACON15*CON1*SA-CON2*SB*ACON16)                                        223
 T13=2.*(ACON14*CON3-ACON12*CON3)*SC                                           224
 T14=2.*CON36*(CON1*AI*SA-CON2*AJ*SB)                                          225
 T15= ACON27*CO                                                                226
 T16=ACON3*ACON27*CO                                                           227
 T17=CON36*ACON27*CO                                                           228
 FU(M)=(T1*HHH*A(1)+(T2*CAB+T3*HH+T4*CAB+T5*U*HH)*A(2)+(T6*(U-2.)+T            229
17+T8*CAB3+T9*CAB2+T10+T11*HH)*A(3)+(T12*CAB*HHH+T13*CAB6+T14*CAB4+            230
2T15*(U-2.)*CAB4)*A(7)+(T16*HHH+T17*CAB2)*A(8))*EAX*AA*.51687084               231
 M=J+672                                                                       232
 U1=CON26*CO                                                                   233
 U2=-CON11*CO                                                                  234
 U3=CON19*AK*SC+CON25*AI*SA                                                    235
 U4=-CON20*AJ*SB-CON25*AI*SA                                                   236
 U5=ACON9*CON10*CB+ACON1*CON11*CO+ACON10*CON4*CA+ACON8*CON12*CC                237
 U6=-ACON9*CON10*CB                                                            238
 U7=-ACON8*CON12*CC                                                            239
 U8=-AK*CON2*SC                                                                240
 U9=AJ*CON3*SB                                                                 241
 U10=ACON12*CON2*SC+ACON20*CON1*SD                                             242
 U11=-ACON20*CON1*SD-ACON11*CON3*SB                                            243
 U12=-ACON10*CA                                                                244
 U13=ACON26*CA                                                                 245
 FU(M)=(U1*HHH*A(1)+(U2+U3*CAB+U4*U)*A(2)*HH+(U5*HH+U6*CAB3+U7*CAB2            246
1+U8*CAB+U9*U)*A(3)+(U10*CAB+U11*U+U12)*A(4)+U13*A(5))*EAX*AA                  247
2*1.19366207                                                                   248
 M=J+768                                                                       249
 E1=CON29*CO                                                                   250
```

```
      E2=AI*CON19*SA-AJ*CON21*SB                                                  251
      E3=AJ*CON7*SB-AI*CON8*SA                                                    252
      E4=ACON27*CON10*CO                                                          253
      E5=ACON8*CON34*CC*U                                                         254
      E6=2.*(AJ*CON1*SB-AI*CON2*SA)                                               255
      E7=ACON4*CON2*SA-ACON5*CON1*SB                                              256
      E8=ACON11*CON1*SB-ACON13*CON2*SA                                            257
      E9=ACON31*CC                                                                258
      FU(M)=(E1*HHH*A(1)+(E2*CIL-E3*U)*HH*A(2)+(-E4*CAB*CER+E5*CIL+E6)*A          259
     1(3)+(E7*CAB+E8*CER)*A(4)+E9*A(5))*EAX*AA*0.59683104                         260
      M=J+864                                                                     261
      H1=CON32*CO                                                                 262
      H2=AK*CON24*SC                                                              263
      H3=-AJ*CON9*SB                                                              264
      H4=CON11*CO                                                                 265
      H5=AK*CON2*SC                                                               266
      H6=-AJ*CON3*SB                                                              267
      H7=ACON3*CON11*CO                                                           268
      H8=ACON10*CON6*CA*U                                                         269
      H9=-CON74*CO                                                                270
      H10=ACON10*CA                                                               271
      H11=ACON6*CON2*SC                                                           272
      H12=ACON16*CON3*SB                                                          273
      H13=(AK*CON2*SC+AJ*CON3*SB)*CON36                                           274
      H14=ACON30*CA                                                               275
      H15=CON36*ACON10*CA                                                         276
      FU(M)=(H1*HHH*A(1)+(H2*HH*CIL+H3*U*HH+H4*(-3.*HH+2.*CAB))*A(2)+(H5          277
     1*CUB+H6*CIL-H7*CAB*CER+H8*CIL+H9)*A(3)+(H10*CUB*CAB4+(H11*CAB+H12          278
     2*CER)*HHH+H13*CAB4)*A(7)+(H14*HHH+H15*CAB2)*A(8))*EAX*AA*1.0337416         279
      M=J+960                                                                     280
      COR63=CON33*CO                                                              281
      COR64=CON23*AK*SC                                                           282
      COR65=-AI*CON9*SA                                                           283
      COR66=CON12*CO                                                              284
      COR67=CON1*AK*SC                                                            285
      COR68=CON3*AI*SA                                                            286
```

```
 COR69=(ACON3*CON12)*CO                                                  287
 COR70=CON6*ACON9*CB*U                                                   288
 COR71=-CON75*CO                                                         289
 COR72=ACON9*CB                                                          290
 COR73=ACON6*CON1*SC                                                     291
 COR74= ACON15*CON3*SA                                                   292
 COR75=CON36*(AK*CON1*SC+AI*CON3*SA)                                     293
 COR76=ACON29*CB                                                         294
 COR77=CON36*ACON9*CB                                                    295
 FU(M)=(COR63*HHH*A(1)+((CIL*COR64+U*COR65)*HH+(-3.0*HH+2.0*CAB)*        296
1COR66)*A(2)+(CUB*COR67-CIL*COR68-CAB*CER*COR69+CIL*COR70+COR71)*       297
2A(3)+((COR72*CUB+COR75)*CAB4+(COR73*CAB+COR74*CER)*HHH)*A(7)+(         298
3COR76*HHH+COR77*CAB2)*A(8))*EAX*AA*1.03374168                          299
 M=J+1056                                                                300
 G1=CON28*CO                                                             301
 G2=CON10*CO                                                             302
 G3=2.*AK*CON25*SC                                                       303
 G4=-AJ*CON23*SB-AI*CON24*SA                                             304
 G5=CON1*AJ*SB+AI*CON2*SA                                                305
 G6=-ACON3*CON10*CO                                                      306
 G7=2.*(ACON10*CON12*CA+ACON9*CON11*CB)                                  307
 G8=-ACON8*CON6*CC                                                       308
 G9=-CON73*CO                                                            309
 G10=ACON8*CC                                                            310
 G11=ACON16*CON1*SB+ACON15*CON2*SA                                       311
 G12=-2.*CON3*ACON20*SD                                                  312
 G13=CON36*(AI*CON2*SA+AJ*CON1*SB)                                       313
 G14=ACON25*CC                                                           314
 G15=CON36*ACON8*CC                                                      315
 FU(M)=(G1*HHH*A(1)+(G2*(CIL+CAB2)+(G3*CAB+G4*U)*HH)*A(2)+(G5*(U-2.      316
1)+ G6*CAB3+G7*HH+G8*CAB2+G9)*A(3)+ ((U-2.)*G10*CAB4+(G11*CAB+G12*U     317
2)*HHH+G13*CAB4)*A(7)+(G14*HHH+G15* CAB2)*A(8))*EAX*AA*1.03374168        318
 M=J+1152                                                                319
 COR10=CON27*CO                                                          320
 COR11=-CON12*CO                                                         321
 COR12=CON21*AK*SC                                                       322
```

```
 COR13=CON22*AI*SA                                                        323
 COR14=CON25*AJ*SB                                                        324
 COR15=CON10*ACON10*CA+CON12*ACON2*CO+CON5*ACON9*CB+CON11*ACON8*CC        325
 COR16=-(CON10*ACON10)*CA                                                 326
 COR17=-(CON11*ACON8)*CC                                                  327
 COR18=-CON1*AK*SC                                                        328
 COR19=CON3*AI*SA                                                         329
 COR20=ACON14*CON1*SC+ACON20*CON2*SD                                      330
 COR21=-ACON20*CON2*SD-ACON13*CON3*SA                                     331
 COR22=-ACON9*CB                                                          332
 COR23=ACON24*CB                                                          333
 FU(M)= (COR10*HHH*A(1)+(COR11+COR12*CAB-COR13*U-COR14*COR     )*HH        334
1*A(2)+(HH*COR15+COR16*CAB3+COR17*CAB2+COR18*CAB+COR19*U)*A(3)+(          335
2COR20+CAB+COR21*U+COR22)*A(4)+COR23*A(5))*EAX*AA*1.19366207              336
 M=J+1248                                                                 337
 F1=CON80*CO                                                              338
 F2=2.*(AI*CON25*SA-AJ*CON22*SB)                                          339
 F3=-CON34*(AJ*CON3*SB+AK*CON2*SC)                                        340
 F4=2.*CON11*CO                                                           341
 F5=2.*AJ*CON3*SB                                                         342
 F6=-2.*AK*CON2*SC                                                        343
 F7=-CON11*ACON27*CO                                                      344
 F8=2.*(ACON8*CON12*CC+ACON9*CON10*CB-ACON2*CON11*CO)                     345
 F9=-ACON10*CON4*CA                                                       346
 F10=-ACON10*CON5*CA*U                                                    347
 F11=ACON11*CON3*SB+ACON12*CON2*SC-ACON14*CON2*SC-ACON5*CON3*SB           348
 F12=-2.*(ACON20*CON1*SD-ACON14*CON2*SC)                                  349
 F13=2.*ACON10*CA                                                         350
 F14=ACON32*CA                                                            351
 FU(M)=(F1*HHH*A(1)+(F2*CAB+F3*U+F4)*HH*A(2)+(F5*CAB+F6*U+F7*CAB3+F       352
18*HH+F9*CAB2+F10*CIL)*A(3)+(F11*CAB+F12*U+F13)*A(4)+F14*A(5))*EAX       353
2*AA*0.59683104                                                          354
 M=J+1344                                                                 355
 COR49=CON81*CO                                                           356
 COR50=2.*(CON20*AI*SA-CON25*AJ*SB)                                       357
 COR51=-CON34*(CON3*AI*SA+CON1*AK*SC)                                     358
```

```
      COR52=2.0*CON12*CO                                                    359
      COR53=-2.0*AI*CON3*SA                                                 360
      COR54=2.0*AK*CON1*SC                                                  361
      COR55=-CON12*ACON27*CO                                                362
      COR56=-2.*(CON11*ACON8*CC+CON10*ACON10*CA-ACON1*CON12*CO)             363
      COR57=ACON9*CON5*CB                                                   364
      COR58=ACON9*CON4*CB*U                                                 365
      COR59=-ACON13*CON3*SA-ACON14*CON1*SC+ACON12*CON1*SC+ACON4*CON3*SA     366
      COR60=2.*(ACON20*CON2*SD-ACON12*CON1*SC)                              367
      COR61=-2.0*ACON9*CB                                                   368
      COR62=ACON34*CB                                                       369
      FU(M)=(COR49*HHH*A(1)+(COR50*CAB+U*COR51-COR52)*HH*A(2)+(CAB*COR53    370
     1+U*COR54+CAB3*COR55+HH*COR56+CAB2*COR57+CIL*COR58)*A(3)+(CAB*COR59    371
     2+U*COR60+COR61)*A(4)+COR62*A(5))*EAX*AA*0.59683104                    372
750   CONTINUE                                                              373
      CALL INTEG                                                            374
      RETURN                                                                375
      END                                                                   376
```

```
C       THIS SUBROUTINE COMPUTES THE KINETIC ENERGY INTEGRALS USING THE          000
C       RELATIONS DEVELOPED BY SLATER AND KOSTER                                 001
        SUBROUTINE NIT(EK,CON1,CON2,CON3,RAB,DDD,DDP,DDS)                        002
        IMPLICIT REAL * 8 ( A - H , O - Z )                                      003
        DIMENSION EK(15)                                                         004
        A=CON1/RAB                                                               005
        B=CON2/RAB                                                               006
        C=CON3/RAB                                                               007
        AA=A*A                                                                   008
        BB=B*B                                                                   009
        CC=C*C                                                                   010
        CON1=3.0*BB*CC                                                           011
        CON1=CON1*DDS                                                            012
        CON2=BB+CC-4.*BB*CC                                                      013
        CON2=CON2*DDP                                                            014
        CON3=AA+BB*CC                                                            015
        CON3=CON3*DDD                                                            016
        EK(4)=CON1+CON2+CON3                                                     017
        CON1=3.*CC*AA                                                            018
        CON1=CON1*DDS                                                            019
        CON2=CC+AA-4.*AA*CC                                                      020
        CON2=CON2*DDP                                                            021
        CON3=BB+AA*CC                                                            022
        CON3=CON3*DDD                                                            023
        EK(3)=CON1+CON2+CON3                                                     024
        CON1=3.*B*CC*A                                                           025
        CON1=CON1*DDS                                                            026
        CON2=B*A*(1.-4.*CC)                                                      027
        CON2=CON2*DDP                                                            028
        CON3=A*B*(CC-1.)                                                         029
        CON3=CON3*DDD                                                            030
        EK(6)=CON1+CON2+CON3                                                     031
        CON1=3.*AA*BB                                                            032
        CON1=CON1*DDS                                                            033
        CON2=AA+BB-4.*AA*BB                                                      034
```

```
CON2=CON2*DDP                                                    035
CON3=CC+AA*BB                                                    036
CON3=CON3*DDD                                                    037
EK(2)=CON1+CON2+CON3                                             038
CON1=3.*A*BB*C                                                   039
CON1=CON1*DDS                                                    040
CON2=A*C*(1.-4.*BB)                                              041
CON2=CON2*DDP                                                    042
CON3=A*C*(BB-1.)                                                 043
CON3=CON3*DDD                                                    044
EK(13)=CON1+CON2+CON3                                            045
CON1=3.*AA*B*C                                                   046
CON1=CON1*DDS                                                    047
CON2=B*C*(1.-4.*AA)                                              048
CON2=CON2*DDP                                                    049
CON3=B*C*(AA-1.)                                                 050
CON3=CON3*DDD                                                    051
EK(8)=CON1+CON2+CON3                                             052
CON1=1.5*A*B*(AA-BB)                                             053
CON1=CON1*DDS                                                    054
CON2=2.*A*B*(BB-AA)                                              055
CON2=CON2*DDP                                                    056
CON3=.5*A*B*(AA-BB)                                              057
CON3=CON3*DDD                                                    058
EK(9)=CON1+CON2+CON3                                             059
CON1=1.5*B*C*(AA-BB)                                             060
CON1=CON1*DDS                                                    061
CON2=-B*C*(1.+2.*(AA-BB))                                        062
CON2=CON2*DDP                                                    063
CON3=B*C*(1.+.5*(AA-BB))                                         064
CON3=CON3*DDD                                                    065
EK(14)=CON1+CON2+CON3                                            066
CON1=1.5*A*C*(AA-BB)                                             067
CON1=CON1*DDS                                                    068
CON2=A*C*(1.-2.*(AA-BB))                                         069
CON2=CON2*DDP                                                    070
```

```
CON3=-A*C*(1.-.5*(AA-BB))                                    071
CON3=CON3*DDD                                                072
EK(15)=CON1+CON2+CON3                                        073
E=DSQRT(3.DO)                                                074
CON1=E*A*B*(CC-.5*(AA+BB))                                   075
CON1=CON1*DDS                                                076
CON2=-2.*E*A*B*CC                                            077
CON2=CON2*DDP                                                078
CON3=.5*E*A*B*(1.+CC)                                        079
CON3=CON3*DDD                                                080
EK(12)=CON1+CON2+CON3                                        081
CON1=E*B*C*(CC-.5*(AA+BB))                                   082
CON1=CON1*DDS                                                083
CON2=E*B*C*(AA+BB-CC)                                        084
CON2=CON2*DDP                                                085
CON3=-.5*E*B*C*(AA+BB)                                       086
CON3=CON3*DDD                                                087
EK(10)=CON1+CON2+CON3                                        088
CON1=E*A*C*(CC-.5*(AA+BB))                                   089
CON1=CON1*DDS                                                090
CON2=E*A*C*(AA+BB-CC)                                        091
CON2=CON2*DDP                                                092
CON3=-.5*E*A*C*(AA+BB)                                       093
CON3=CON3*DDD                                                094
EK(11)=CON1+CON2+CON3                                        095
CON1=.75*(AA-BB)**2                                          096
CON1=CON1*DDS                                                097
CON2=AA+BB-(AA-BB)**2                                        098
CON2=CON2*DDP                                                099
CON3=CC+.25*(AA-BB)**2                                       100
CON3=CON3*DDD                                                101
EK(5)=CON1+CON2+CON3                                         102
CON1=.5*E*(AA-BB)*(CC-.5*(AA+BB))                            103
CON1=CON1*DDS                                                104
CON2=E*CC*(BB-AA)                                            105
CON2=CON2*DDP                                                106
```

```
CON3=.25*E*(1.+CC)*(AA-BB)                                    107
CON3=CON3*DDD                                                 108
EK(7)=CON1+CON2+CON3                                          109
CON1=(CC-.5*(AA+BB))**2                                       110
CON1=CON1*DDS                                                 111
CON2=3.*CC*(AA+BB)                                            112
CON2=CON2*DDP                                                 113
CON3=.75*(AA+BB)**2                                           114
CON3=CON3*DDD                                                 115
EK(1)=CON1+CON2+CON3                                          116
RETURN                                                        117
END                                                           118
```

```
      SUBROUTINE SZE(E,ZA,ZB,NA,LA,MA,XA,CA,NB,LB,MB,XB,CB,ABK,INDA,AFUN      000
     1)                                                                       001
      IMPLICIT REAL * 8 ( A - H  ,  O - Z )                                   002
      COMMON/CFUN/P(40),Q(40),R(40),D(9),DX,SCRAP(150),FAA(10),FBB(10),O      003
     *O/FACL/BF(100)                                                          004
      DIMENSION INDA(5,5,5),AFUN(9,9,55)                                      005
C                                                                             006
C     FUNCTION SZE IS SET UP TO CALCULATE THE ONE-ELECTRON INTEGRALS           007
C     (NA,LA,MA,XA/OP/NB,LB,MB,XB) , WHERE OP IS THE OPERATOR FOR             008
C     RESPECTIVELY - OVERLAP,KINETIC ENERGY,AND EXCHANGE NUCLEAR              009
C     ATTRACTION (RA**-1 AND RB**-1)                                          010
C     THE PARAMETERS ARE--                                                    011
C     E        KINETIC ENERGY INTEGRAL                                        012
C     ZA       NUCLEAR ATTRACTION  (A/RA**-1/B)*CA                            013
C     ZB       NUCLEAR ATTRACTION  (A/RB**-1/B)*CB                            014
C     NA,LA,MA,XA,CA          ARE RESPECTIVELY THE DEFINING QUANTUM NOS.     015
C                             ORBITAL EXPONENT AND CORE CHARGE FOR A         016
C     NB,LB,MB,XB,CB          DITTO FOR CENTRE B                             017
C     ABK IS THE FACTOR KAB FROM THE PAPERS BY N.M.KLIMENKO AND M.E.          018
C     DYATKINA IN J.STRUCT.CHEM. (ENGLISH TRANSLATION) VOL.6.,573 AND         019
C     714(1965).                                                              020
C     THE ALGORITHM IS ESSENTIALLY THAT OUTLINED BY THEM,BUT MODIFIED TO      021
C     TAKE ADVANTAGE OF SIMILARITIES IN THE REQUIRED C-FUNCTIONS.             022
C     NOTE THAT THE ONE CENTRE NUCLEAR ATTRACTION INTEGRAL IS NON-ZERO        023
C     IN ZA,ZERO IN ZB.                                                       024
C                                                                             025
      E  = 0.0                                                                026
      ZA = 0.0                                                                027
      ZB = 0.0                                                                028
      INIT=0                                                                  029
      IF(MA-MB)1000,20,1000                                                   030
   20 IF(OD)60,40,60                                                          031
   40 IF(LA-LB)1000,60,1000                                                   032
   60 M=IABS(MA)                                                              033
      V=XA/XB                                                                 034
```

```
      V1=V**(NA+0.5)                                                    035
      V2=V1/V                                                           036
      V3=V2/V                                                           037
      FACS=ABK*V1                                                       038
      FACE=-0.5*XA*XA*ABK                                               039
      FACZA=XA*ABK*V2                                                   040
      FACZB=-FACZA*CB                                                   041
      FACZA=-FACZA*CA                                                   042
      FACE1=V1                                                          043
      FACE2=-V2*(NA+NA)                                                 044
      NL1=NA-LA-1                                                       045
      IF(NL1)100,100,80                                                 046
   80 FACE3=(NA+LA)*NL1*V3                                              047
      LF=3                                                              048
      GO TO 120                                                         049
  100 FACE3=0.                                                          050
      LF=2                                                              051
  120 LAM=LA-M                                                          052
      LBM=LB-M                                                          053
      LAM1=LAM-1                                                        054
      LBM1=LBM-1                                                        055
      FAA(1) = 1.                                                       056
      FBB(1) = 1.                                                       057
      LIMA = 0                                                          058
      LIMB = 0                                                          059
      IF(LAM1)160,160,140                                               060
  140 FAA(2) = -1.D+00 * LAM * LAM1 / ( 4.D+00 * LA - 2.D+00 )          061
      LIMA=1                                                            062
  160 IF(LBM1)200,200,180                                               063
  180 FBB(2) = -1.D+00 * LBM * LBM1 / ( 4.D+00 * LB - 2.D+00 )          064
      LIMB=1                                                            065
  200 NAB=NA+NB                                                         066
      LAB=LA+LB                                                         067
      IF(OD)300,300,500                                                 068
C     RO ZERO                                                           069
  300 XX=XB/(XA+XB)                                                     070
```

```
      DX=0.                                                              071
      IF1=LAM+LBM+1                                                      072
      JF1=LAB/2+1                                                        073
      KF1=(LAM+LBM)/2+1                                                  074
      LF1=LAB+2                                                          075
      DO 320 KA=INIT,LIMA                                                076
      FA=FAA(KA+1)                                                       077
      KA2=KA+KA                                                          078
      IF2=IF1-KA2                                                        079
      JF2=JF1-KA                                                         080
      KF2=KF1-KA                                                         081
      LF2=LF1-KA2                                                        082
      DO 320 KB=INIT,LIMB                                                083
      FB=FBB(KB+1)*FA                                                    084
      KB2=KB+KB                                                          085
      IF3=IF2-KB2                                                        086
      JF3=JF2-KB                                                         087
      KF3=KF2-KB                                                         088
      LF3=LF2-KB2                                                        089
  320 DX=DX+FB*BF(IF3)*BF(JF3)/(BF(KF3)*BF(LF3))                         090
      NAB2=NAB+2                                                         091
      DX=DX*2.**(M+M+1)*BF(M+1)*XX**NAB2                                 092
  360 DO 380 I1=1,LF                                                     093
      DX=DX/XX                                                           094
  380 D(I1)=DX*BF(NAB2-I1)                                               095
  400 ZA=FACZA*D(2)                                                      096
      E=FACE1*D(1)+FACE2*D(2)                                            097
      IF(FACE3)420,440,420                                               098
  420 E=E+FACE3*D(3)                                                     099
  440 E=E*FACE                                                           100
      GO TO 1000                                                         101
C     RO NON-ZERO                                                        102
C500  D(1)=D(2)=D(3)=DB=0.                                               103
  500 D(1) = 0.0                                                         104
      D(2) = 0.0                                                         105
      D(3) = 0.0                                                         106
```

```
DB    = 0.0                                                          107
RB=XB*OD                                                             108
RA=XA*OD                                                             109
RO=RA+RB                                                             110
IF(RO.GT.160.)GO TO 1000                                             111
RT=RA-RB                                                             112
EPRB = DEXP ( RB )                                                   113
ENRB=1./EPRB                                                         114
NMAX=NAB+LAB                                                         115
NMIN=0                                                               116
IREF=1-NMIN                                                          117
CALL PCRN(RO,RT,NMIN,NMAX,P,Q,R,BF,IREF)                             118
N1=NA-LA+IREF                                                        119
LAM1=LAM+1                                                           120
LBM1=LBM+1                                                           121
M1=M+1                                                               122
NLB=NB-LB                                                            123
DO 900 KA=INIT,LIMA                                                  124
KA2=KA+KA                                                            125
FA=FAA(KA+1)                                                         126
LAM2=LAM1-KA2                                                        127
LR1=LAB-KA2                                                          128
N2=N1+KA2                                                            129
DO 900 KB=INIT,LIMB                                                  130
KB2=KB+KB                                                            131
FB=FA*FBB(KB+1)                                                      132
LBM2=LBM1-KB2                                                        133
NLB1=NLB+KB2                                                         134
LR=LR1-KB2                                                           135
IND=INDA(LAM2,LBM2,M1)                                               136
DO 900 IR=INIT,LR                                                    137
IR1=IR+1                                                             138
IR2=IR+IR                                                            139
N3=N2+IR2                                                            140
LS=LR-IR                                                             141
DO 880 IS=INIT,LS                                                    142
```

```
      IS1=IS+1                                                          143
      IS2=IS+IS                                                         144
      AA=AFUN(IR1,IS1,IND)                                              145
      IF(AA)520,880,520                                                 146
520   FC=FB*AA                                                          147
      LK=NLB1+IS2                                                       148
      FC2=FC*BF(LK)                                                     149
      FC1=FC*BF(LK+1)                                                   150
      FD=FC1                                                            151
      N4=N3+1                                                           152
      DO 700 IK=INIT,LK                                                 153
      FD=FD/RB                                                          154
      LL=LK-IK                                                          155
      DO 700 IL=INIT,LL                                                 156
      LLL=LL-IL                                                         157
      FE=FD/(BF(IL+1)*BF(LLL+1))                                        158
      N5=N4+IL                                                          159
      FP = 1.                                                           160
      FR = 1.                                                           161
      IF(LLL/2*2-LLL)600,620,600                                        162
600   FP=-1.                                                            163
620   IF(IL/2*2-IL)640,660,640                                          164
640   FR=-1.                                                            165
660   DO 700 IF=1,LF                                                    166
      N=N5-IF                                                           167
700   D(IF)=D(IF)+FE*(FP*EPRB*P(N)+ENRB*(FR*R(N)-Q(N)))                 168
      N4=N3                                                             169
      FD=FC2                                                            170
      LK=LK-1                                                           171
      DO 800 IK=INIT,LK                                                 172
      FD=FD/RB                                                          173
      LL=LK-IK                                                          174
      DO 800 IL=INIT,LL                                                 175
      LLL=LL-IL                                                         176
      FE=FD/(BF(IL+1)*BF(LLL+1))                                        177
      N=N4+IL                                                           178
```

```
      FP = 1.                                                          179
      FR = 1.                                                          180
      IF(LLL/2*2-LLL)720,740,720                                       181
720   FP=-1.                                                           182
740   IF(IL/2*2-IL)760,800,760                                         183
760   FR=-1.                                                           184
800   DB=DB+FE*(FP*EPRB*P(N)+ENRB*(FR*R(N)-Q(N)))                      185
880   CONTINUE                                                         186
900   CONTINUE                                                         187
      FD=RB**NAB                                                       188
      DB=DB*FD                                                         189
      FD=FD*RB                                                         190
      D(1)=D(1)*FD                                                     191
      DO 920 KA=2,LF                                                   192
      FD=FD/RB                                                         193
920   D(KA)=D(KA)*FD                                                   194
      ZB=FACZb*DB                                                      195
      GO TO 400                                                        196
1000  RETURN                                                           197
      END                                                              198
```

```
      SUBROUTINE FACGEN(BF)                                                  000
      IMPLICIT REAL * 8 ( A - H , O - Z )                                    001
C        **  THIS SUBROUTINE HAS BEEN CHANGED FROM 100 TO 57  JHRS  **       002
C     FACTORIAL GENERATOR                                                    003
      DIMENSION BF(100)                                                      004
      BF(1)=1.                                                               005
C     DO 10 I=1,99                                                           006
      DO 10 I=1,56                                                           007
 10   BF(I+1)=I*BF(I)                                                        008
C                                                                            009
      DO 20 I = 57 , 94 , 5                                                  010
      BF(I+1) = + 10.D-78                                                    011
      BF(I+2) = - 10.D+63                                                    012
      BF(I+3) =    0.D+00                                                    013
      BF(I+4) = - 10.D-78                                                    014
      BF(I+5) = + 10.D+63                                                    015
 20   CONTINUE                                                               016
      RETURN                                                                 017
      END                                                                    018
```

```
      SUBROUTINE AGENT(INDA,AFUN)                                       000
      IMPLICIT REAL * 8 ( A - H  ,  O - Z )                             001
      COMMON/FACL/BF(100)                                               002
      DIMENSION INDA(5,5,5),AFUN(9,9,55)                                003
      INIT = 0                                                          004
      N    = 0                                                          005
      DO 100 M=INIT,4                                                   006
      MM=M+1                                                            007
      LIM=4-M                                                           008
      DO 100 K=INIT,LIM                                                 009
      KK=K+1                                                            010
      DO 100 L=INIT,LIM                                                 011
      LL=L+1                                                            012
      N=N+1                                                             013
      INDA(KK,LL,MM)=N                                                  014
      LIMR=K+L+M+M                                                      015
      DO 100 IR=INIT,LIMR                                               016
      JR=IR+1                                                           017
      LIMS=LIMR-IR                                                      018
      DO 100 IS=INIT,LIMS                                               019
      JS=IS+1                                                           020
      AA=A(IR,IS,K,L,M)                                                 021
      IF(DABS(AA)-1.E-8)90,90,100                                       022
90    AA=0.                                                             023
100   AFUN(JR,JS,N)=AA                                                  024
      RETURN                                                            025
      END                                                               026
```

```
      SUBROUTINE PQRN(RO,RT,NMIN,NMAX,P,Q,R,BF,IREF)                    000
      IMPLICIT REAL * 8 ( A - H , O - Z )                               001
      DIMENSION P(40),Q(40),R(40),BF(100)                               002
      NMINA=IABS(NMIN)                                                  003
      IREF=NMINA+1                                                      004
      RON=-RO                                                           005
      ER = DEXP ( RON )                                                 006
      NMINA1=NMINA-1                                                    007
C     PN,QN BY FORWARD RECURRENCE    ALL N.GT.0,ALL RO.GT.0             008
      P(IREF) = ER / RO                                                 009
      PP      = ER / RO                                                 010
      Q(IREF) = 1.0D+00 / RO                                            011
      RRO     = 1.0D+00 / RO                                            012
      IF(NMAX)50,50,20                                                  013
   20 DO 40 I=1,NMAX                                                    014
      RR=RRO*I                                                          015
      IRI=IREF+I                                                        016
      P(IRI)=PP+RR*P(IRI-1)                                             017
   40 Q(IRI)=RR*Q(IRI-1)                                                018
   50 IF(NMIN)60,480,480                                                019
C     PN,QN   N.LT.0                                                    020
   60 IF(RO-4.)80,300,300                                               021
C     PN BY FORWARD RECURRENCE EX PO    N.LT.0,RO.LT.4                  022
   80 CALN=DLOG(RO)+0.577215664901533                                   023
      IF(RO-1.)100,140,140                                              024
  100 NT=10.-DLOG10(RO)                                                 025
      IF(NT-5)120,160,160                                               026
  120 NT=5                                                              027
      GO TO 160                                                         028
  140 NT=6.*RO+11.                                                      029
C     EI BY SERIES EXPANSION                                            030
  160 TB = RON                                                          031
      EI = RON                                                          032
      DO 180 I=2,NT                                                     033
      TB=TB*RON/I                                                       034
```

```
 180  EI=EI+TB/I                                                        035
      EI=EI+CALN                                                        036
      P(IREF-1)=-EI                                                     037
      Q(IREF-1)=-CALN                                                   038
      IF(NMINA)480,480,200                                              039
C     PN  FORWARD RECURRENCE,SET Q ARRAY TO ZERO                        040
 200  DO 220 N=2,NMINA                                                  041
      IRN=IREF-N                                                        042
      Q(IRN)=0.                                                         043
 220  P(IRN)=(ER-RO*P(IRN+1))/(N-1.)                                    044
C     ENTRY FOR QN CALCULATION,WITH Q(-1) SET,OTHERS ZERO               045
 240  Q2=1.                                                             046
      F1=RO                                                             047
      Q(IREF-2)=F1*(CALN-Q2)+Q2                                         048
      IF(NMINA-2)480,480,260                                            049
 260  DO 280 I=3,NMINA                                                  050
      IRI=IREF-I                                                        051
      Q3 = 1.D+00 / ( I - 2. )                                          052
      XI = 1.D+00 / ( I - 1. )                                          053
      F1=F1*RON*XI                                                      054
      Q2=Q2+XI                                                          055
      Q(IRI)=Q(IRI)+F1*(CALN-Q2)+XI                                     056
      DO 280 J=I,NMINA                                                  057
      IRJ=IREF-J                                                        058
      Q3=Q3*RON/(J-I+1.)                                                059
 280  Q(IRJ)=Q(IRJ)+Q3                                                  060
      GO TO 480                                                         061
C     PN BY BACK RECURRENCE EX CONTINUED FRACTION    N.LT.0,RO.GE.4     062
 300  IF(RO-100.)340,340,320                                            063
 320  NT=-5                                                             064
      GO TO 400                                                         065
 340  IF(RO-6.)380,360,360                                              066
 360  NT=-100./RO-6.                                                    067
      GO TO 400                                                         068
 380  NT=-24                                                            069
 400  NL=-1                                                             070
```

```
      CF=0.                                                              071
      DO 420 I=NT,NL                                                     072
      CC=1.+CF                                                           073
  420 CF=-I*CC/(RO*CC+NMINA-I)                                           074
      P(1)=ER*(1.+CF)/(RO*(1.+CF)+NMINA)                                 075
C     SET Q(-1)                                                          076
      CALN=DLOG(RO)+0.577215664901533                                    077
      Q(IREF-1)=-CALN                                                    078
      IF(NMINA1)480,480,440                                              079
C     PN  BACK RECURRENCE,SET Q ARRAY TO ZERO                            080
  440 DO 460 I=2,NMINA                                                   081
      IRN=I-IREF                                                         082
      P(I)=(ER+IRN*P(I-1))/RO                                            083
  460 Q(-IRN)=0.                                                         084
      GO TO 240                                                          085
C     START ON RN CALCULATION    FIRSTLY,IS TAU ZERO                     086
  480 IF(RT)580,500,580                                                  087
C     RN=1/(N+1)  FOR N.GT.0                                             088
  500 R(IREF)=1.                                                         089
      IF(NMAX)530,530,510                                                090
  510 DO 520 I=1,NMAX                                                    091
  520 R( IREF + I ) = 1.D+00 / ( I + 1. )                                092
  530 IF(NMIN)540,3000,3000                                              093
  540 DO 560 I=1,NMINA                                                   094
  560 R(I)=0.                                                            095
      GO TO 3000                                                         096
C     SORT OUT VALUES OF RT FOR RN(N.GE.0)                               097
  580 ART = DABS ( RT  )                                                 098
      RTN=-RT                                                            099
      ERT = DEXP ( RTN )                                                 100
      IF(RT-80.)680,600,600                                              101
C     RN=QN    FOR N.GE.0,RT.GE.80                                       102
  600 RRT     = 1.D+00 / RT                                              103
      R(IREF) = RRT                                                      104
      IF(NMAX)660,660,620                                                105
  620 DO 640 I=1,NMAX                                                    106
```

```
      IRI=IREF+I                                                        107
  640 R(IRI)=ERT*R(IRI-1)*I                                             108
  660 IF(NMIN)1200,3000,3000                                            109
  680 IF(RT-9.)780,700,700                                              110
C     RN BY DYATKINA     N.GE.0,9.GE.RT.LT.80 AND -40.GT.RT.LE.-8       111
  700 R1=1./RT                                                          112
      R2=ERT/RT                                                         113
      R(IREF)=R1-R2                                                     114
      IF(NMAX)760,760,720                                               115
  720 DO 740 I=1,NMAX                                                   116
      IRI=IREF+I                                                        117
  740 R(IRI)=R1*(I*R(IRI-1)-ERT)                                        118
  760 GO TO 1160                                                        119
  780 IF(RT)960,960,800                                                 120
C     ESTABLISH LIMIT FOR RN AS SERIES     N.GE.0,0.GE.RT.LT.9        121
  800 IF(RT-1.)820,860,860                                              122
  820 NT=2.*DLOG10(ART)+13.                                             123
      IF(NT-7)840,880,880                                               124
  840 NT=7                                                              125
      GO TO 880                                                         126
  860 NT=2.8*ART+19.-NMAX*(ART+6.)/18.                                  127
  880 F1 = ERT / ( NMAX + 1. )                                          128
      A1 = F1                                                           129
      K=NMAX+2                                                          130
      KK=NMAX+NT                                                        131
      DO 900 J=K,KK                                                     132
      F1=F1*RT/J                                                        133
  900 A1=A1+F1                                                          134
      R(IREF+NMAX)=A1                                                   135
      IF(NMAX)1160,1160,920                                             136
C     RN    BACK RECURRENCE                                             137
  920 NNM=-NMAX                                                         138
      LIM=-1                                                            139
      DO 940 I=NNM,LIM                                                  140
      IRI=IREF-I                                                        141
  940 R(IRI-1)=(RT*R(IRI)+ERT)/(-1)                                     142
```

```
      GO TO 1160                                                        143
  960 IF(RT+8.)1080,10EC,980                                            144
C     ESTABLISH LIMIT FOR RN AS SERIES    N.GE.0,-8.GT.RT.LT.0          145
  980 IF(RT+0.01)1020,1020,1000                                         146
 1000 NT=6                                                              147
      GO TO 880                                                         148
 1020 IF(RT+1.)1060,1060,1040                                           149
 1040 NT=18.+6.*DLOG10(ART)                                             150
      GO TO 880                                                         151
 1060 NT=ART*(5.036-0.131*ART)+14.+0.1*(NMAX*RT-40.)                    152
      GO TO 880                                                         153
 1080 IF(RT+40.)1100,1100,700                                           154
C     RN=PN     N.GE.0,RT.LE.-40                                        155
 1100 PP       = - ERT / RT                                             156
      R(IREF) = PP                                                      157
      IF(NMAX)1160,1160,1120                                            158
 1120 RR=1./RT                                                          159
      DO 1140 I=1,NMAX                                                  160
      IRI=IREF+I                                                        161
 1140 R(IRI)=PP+RR*I*R(IRI-1)                                           162
C     FINIS OF RN,N.GE.0   START NOW ON N.LT.0                          163
 1160 IF(NMIN)1180,3000,3000                                            164
 1180 IF(RT-40.)1300,1200,1200                                          165
C     RN=QN   N.LT.0,RT.GE.40                                           166
 1200 CALN=DLOG(ART)+0.577215664901533                                  167
      R(IREF-1)=-CALN                                                   168
      IF(NMINA1)3000,3000,1220                                          169
 1220 DO 1240 I=2,NMINA                                                 170
      IRN=IREF-I                                                        171
 1240 R(IRN)=0.                                                         172
      R2=1.                                                             173
      F1=RT                                                             174
      R(IREF-2)=F1*(CALN-R2)+R2                                         175
      IF(NMINA-2)3000,3000,1260                                         176
 1260 DO 1280 I=3,NMINA                                                 177
      IRI=IREF-I                                                        178
```

```
      R3 = 1.D+00 / ( I - 2. )                                          179
      XI = 1.D+00 / ( I - 1. )                                          180
      F1=F1*RTN*XI                                                      181
      R2=R2+XI                                                          182
      R(IRI)=R(IRI)+F1*(CALN-R2)+XI                                     183
      DO 1280 J=I,NMINA                                                 184
      IRJ=IREF-J                                                        185
      R3=R3*RTN/(J-I+1.)                                                186
 1280 R(IRJ)=R(IRJ)+R3                                                  187
      GO TO 3000                                                        188
 1300 IF(RT-2.)1500,1320,1320                                           189
C     ESTABLISH LIMITS FOR EI(CONTINUED FRACTION) IN RN BY DYATKINA     190
C     N.LT.0,2.GE.RT.LT.60                                              191
 1320 IF(RT-6.)1360,1360,1340                                           192
 1340 NT=-100./ART-6.                                                   193
      GO TO 1380                                                        194
 1360 NT=-24                                                            195
 1380 NL=-1                                                             196
      CF=0.                                                             197
      DO 1400 I=NT,NL                                                   198
      CC=1.+CF                                                          199
 1400 CF=-I*CC/(RT*CC+1-I)                                              200
      CF=-ERT*(1.+CF)/(RT*(1.+CF)+1.)                                   201
      CALNEI=0.577215664901533+DLOG(ART)-CF                             202
      R(IREF-1)=-CALNEI                                                 203
      IF(NMINA1)3000,3000,1420                                          204
 1420 R(IREF-2)=RT*(CALNEI-1.)+1.-ERT                                   205
      IF(NMINA-2)3000,3000,1440                                         206
 1440 T1=1.                                                             207
      F1=RT                                                             208
      DO 1480 I=3,NMINA                                                 209
      T4 = 1.D+00 / ( I - 1. )                                          210
      A  = T4                                                           211
      XI = T4                                                           212
      F1=F1*RTN*XI                                                      213
      T1=T1+XI                                                          214
```

```
      AA=1.                                                              215
      T3=0.                                                              216
      I2=I-2                                                             217
      DO 1460 J=1,I2                                                     218
      BB=I-J-1.                                                          219
      A=A*RTN/BB                                                         220
      AA=AA*RTN/J                                                        221
      T4=T4+A                                                            222
 1460 T3=T3+AA/BB                                                        223
 1480 R(IREF-I)=F1*(CALNEI-T1)+T3+XI-ERT*T4                              224
      GO TO 3000                                                         225
 1500 IF(RT+2.)1700,1700,1520                                            226
C     RN BY SERIES,ALL N.LT.0,  -2.GT.RT.LT.2,RT.NE.0                    227
 1520 IF(ART-0.1)1540,1580,1580                                          228
 1540 NT=10-DLOG10(ART)                                                  229
      IF(NT-5)1560,1600,1600                                             230
 1560 NT=5                                                               231
      GO TO 1600                                                         232
 1580 NT=6.*ART+11.                                                      233
 1600 TA=1.                                                              234
      DO 1620 N=1,NMINA                                                  235
      TA=TA/N                                                            236
 1620 R(IREF-N)=RTN*TA                                                   237
      TA=RTN                                                             238
      DO 1640 I=2,NT                                                     239
      I1=I-1                                                             240
      TA=TA*RTN/I1                                                       241
      TB=TA/I                                                            242
      DO 1640 N=1,NMINA                                                  243
      IRN=IREF-N                                                         244
      TB=TB/(I1+N)                                                       245
 1640 R(IRN)=R(IRN)+TB                                                   246
      IF(NMINA1)3000,3000,1660                                           247
C     FINISH OFF RN  BY SERIES                                           248
 1660 TA=1.                                                              249
      DO 1680 N=2,NMINA                                                  250
```

```
      IRN=IREF-N                                                        251
      TA=TA*RTN                                                         252
 1680 R(IRN)=R(IRN)*TA                                                  253
      GO TO 3000                                                        254
 1700 IF(RT+60.)1980,1980,1760                                          255
C     RN BY MIXED FORMULA   FIRSTLY CALCULATE RN FOR MOST NEGATIVE N    256
C     NEXT,CALCULATE QN IN R ARRAY,ALL N,N.LT.0                         257
C     THEN,PN=QN-RN FOR MOST NEGATIVE N,AND BACK RECURRENCE OF PN       258
C     (STABLE) GIVES RN BY QN-PN                                        259
 1760 NDEC=NMIN                                                         260
      IF(RT+4.)1800,1800,1780                                           261
 1780 NDEC=NMIN/2                                                       262
 1800 NT=ART*(2.981-0.0215*ART)+19.+NDEC                                263
      F1 = 1.                                                           264
      A1 = 1.                                                           265
      DO 1820 I=2,NT                                                    266
      F1=F1*RTN/(NMINA1+I)                                              267
 1820 A1=A1+F1/I                                                        268
      RR=A1*RTN**NMINA/BF(IREF)                                         269
      IF(NMINA1)1940,1840,1860                                          270
 1940 R(1)=RR                                                           271
      GO TO 3000                                                        272
C     PUT QN INTO R ARRAY                                               273
 1860 DO 1880 I=1,NMINA                                                 274
 1880 R(I)=0.                                                           275
      CALN=DLOG(ART)+0.577215664901533                                  276
      R(IREF-1)=-CALN                                                   277
      R2=1.                                                             278
      F1=RT                                                             279
      R(IREF-2)=F1*(CALN-R2)+R2                                         280
      IF(NMINA-2)1940,1940,1900                                         281
 1900 DO 1920 I=3,NMINA                                                 282
      IRI=IREF-I                                                        283
      R3 = 1.D+00 / ( I - 2. )                                          284
      XI = 1.D+00 / ( I - 1. )                                          285
      F1=F1*RTN*XI                                                      286
```

```
      R2=R2+XI                                                                  287
      R(IRI)=R(IRI)+FI*(CALN-R2)+XI                                             288
      DO 1920 J=I,NMINA                                                         289
      IRJ=IREF-J                                                                290
      R3=R3*RTN/(J-I+1.)                                                        291
 1920 R(IRJ)=R(IRJ)+R3                                                          292
C     BACK RECURRENCE FOR PN AS PP                                              293
 1940 PP=R(1)-RR                                                                294
      R(1)=RR                                                                   295
      DO  960 I=2,NMINA                                                         296
      IRN=I-IREF                                                                297
      PP=(ERT+IRN*PP)/RT                                                        298
 1960 R(I)=R(I)-PP                                                              299
      GO TO 3000                                                                300
C     RN=PN  N.LT.0,  RT.LE.-60  PN BY CONTINUED FRACTION AND BACK REC.         301
 1980 NT=-7                                                                     302
      NL=-1                                                                     303
      CF=0.                                                                     304
      DO 2000 I=NT,NL                                                           305
      CC=1.+CF                                                                  306
 2000 CF=-I*CC/(RT*CC+NMINA-I)                                                  307
      R(1)=-ERT*(1.+CF)/(RT*(1.+CF)+NMINA)                                      308
      IF(NMINA1)3000,3000,2020                                                  309
 2020 DO 2040 I=2,NMINA                                                         310
      IRN=I-IREF                                                                311
 2040 R(I)=(-ERT+IRN*R(I-1))/RT                                                 312
 3000 RETURN                                                                    313
      END                                                                       314
```

```
      DOUBLE PRECISION FUNCTION A ( IR , IS , IT , JT , MT )                    000
      IMPLICIT REAL * 8 ( A - H  ,  O - Z )                                     001
      COMMON/FACL/BF(100)                                                       002
      A=0.                                                                      003
      INIT=0                                                                    004
      DO 420 I2=INIT,IT                                                         005
      IR1=IR-I2                                                                 006
      IF(IR1)440,20,20                                                          007
20    IL3=IT-I2                                                                 008
      F1=BF(I2+1)                                                               009
      DO 400 I3=INIT,IL3                                                        010
      IS1=IS-I3                                                                 011
      IF(IS1)420,40,40                                                          012
40    I1=IL3-I3                                                                 013
      F2=F1*BF(I3+1)*BF(I1+1)                                                   014
      DO 380 J2=INIT,JT                                                         015
      IR2=IR1-J2                                                                016
      IF(IR2)400,60,60                                                          017
60    JL3=JT-J2                                                                 018
      F3=F2*BF(J2+1)                                                            019
      I3J2=I3+J2                                                                020
      DO 360 J3=INIT,JL3                                                        021
      IS2=IS1-J3                                                                022
      IF(IS2)380,80,80                                                          023
80    J1=JL3-J3                                                                 024
      F4=F3*BF(J3+1)*BF(J1+1)                                                   025
      DO 340 M2=INIT,MT                                                         026
      IR3=IR2-M2                                                                027
      IF(IR3)360,100,100                                                        028
100   LM3=MT-M2                                                                 029
      F5=F4*BF(M2+1)                                                            030
      DO 320 M3=INIT,LM3                                                        031
      IS3=IS2-M3                                                                032
      IF(IS3)340,120,120                                                        033
120   LM4=LM3-M3                                                                034
```

```
      F6=F5*BF(M3+1)                                                    035
      M23=M2+M3                                                         036
      DO 300 M4=INIT,LM4                                                037
      IR4=IR3-M4                                                        038
      IF(IR4)320,140,140                                                039
140   IS4=IS3-M4                                                        040
      IF(IS4)320,160,160                                                041
160   LM5=LM4-M4                                                        042
      F7=F6*BF(M4+1)                                                    043
      M234=M23+M4                                                       044
      DO 280 M5=INIT,LM5                                                045
      IR5=IR4-M5-M5                                                     046
      IF(IR5)300,180,280                                                047
180   LM6=LM5-M5                                                        048
      F8=F7*BF(M5+1)                                                    049
      DO 260 M6=INIT,LM6                                                050
      IS5=IS4-M6-M6                                                     051
      IF(IS5)280,200,260                                                052
200   M1=LM6-M6                                                         053
      F9=F8*BF(M6+1)*BF(M1+1)                                           054
      AA=2.**M234/F9                                                    055
      NEG=M234+13J2                                                     056
      IF(NEG/2*2-NEG)220,240,220                                        057
220   AA=-AA                                                            058
240   A=A+AA                                                            059
260   CONTINUE                                                          060
280   CONTINUE                                                          061
300   CONTINUE                                                          062
320   CONTINUE                                                          063
340   CONTINUE                                                          064
360   CONTINUE                                                          065
380   CONTINUE                                                          066
400   CONTINUE                                                          067
420   CONTINUE                                                          068
440   A=A*BF(IT+1)*BF(JT+1)*BF(MT+1)/2.**(IT+JT+MT+MT)                  069
      IF(MT/2*2-MT)460,480,460                                          070
```

```
460   A=-A                                                    071
480   RETURN                                                  072
      END                                                     073
```

```
C                                                                       000
C     $ $ $ $ $ $ $ $ $ $ $ MAIN PROGRAM VANSS * * * * * * * * * * * * 001
C                                                                       002
      IMPLICIT REAL*8(A-F,H,O-Z)                                        003
      DIMENSION RK(500),B(500),C(500),D(500),IOU(500),ALD(11),CD(44),VK( 004
     1500)                                                              005
      DIMENSION SS(10),INDA(125),AFUN(4455)                             006
      DIMENSION SUM(10),SOL1(10),SUM1(10),COJ(10),EK(10)                007
      DIMENSION SOLD(10),CDC(16),IEX(11)                                008
      DIMENSION S  (20)                                                 009
      DIMENSION GER(20),SINT(2)                                         010
      DIMENSION FU(100) ,A(9),W(96),V(96)                               011
      COMMON/CFUN/XXX(300),OD/FACL/BF(100)                              012
     1/BIGS/ CON35,CON36,CON38,CON39,CON40,CON41,CON42,CON43,CON44,CON45 013
     1,CON46,CON47,CON48,CON49,CON50,CON51,CON52,CON53,CON54,CON55,CON56 014
     2,CON57,CON58,S,W,V,U,A,RAB,ALPHA1,ALPHA2,RS,FU,AI,AJ,AK,AX,AY,AZ, 015
     38X,BY,BZ,CX,CY,CZ,AA,N,IE,IX                                      016
C                                                                       017
C     THIS PROGRAM COMPUTES POTENTIAL,KINETIC ENERGY,EXCHANGE,AND OVERLA 018
C     INTEGRALS BETWEEN FUNCTIONS OF S SYMMETRY FROM 1S THROUGH 4S      019
C                                                                       020
C                                                                       021
C     AT THIS POINT INSERT V(I) AND W(J) FROM MAIN PROGRAM VANDD,       022
C     LINES 026 THROUGH 217                                             023
C                                                                       024
C                                                                       025
C     READ OR WRITE THE FILE IDENTIFICATION ON THE TAPE                 026
C     WRITE(3,16)                                                       027
C  16 FORMAT(1X,'SS INTEGRALS VV')                                      028
C                                                                       029
      READ(3,16)(GER(N),N=1,4)                                          030
   16 FORMAT(4A4)                                                       031
      KJ=1                                                              032
      READ(5,6)(GER(I),I=1,20)                                          033
    6 FORMAT(20A3)                                                      034
```

```
C      READ NUMBER OF TERMS TO BE INCLUDED IN FOURIER SERIES                    035
       READ(5,101)JJJJ                                                          036
  101  FORMAT(I5)                                                               037
C      PARAMETER KKR                                                            038
C         1 COMPUTE EXCHANGE ONLY                                               039
C         2 COMPUTE POTENTIAL ONLY                                              040
C         3 COMPUTE POTENTIAL AND EXCHANGE                                      041
       READ(5,101)KKR                                                           042
C      READ A/2                                                                 043
       READ(5,641)QA                                                            044
  641  FORMAT(F9.6)                                                             045
       GOTO (17,11,11),KKR                                                      046
C      READ FOURIER COEFFICIENTS OF POTENTIAL                                   047
C      THE FOURIER SERIES SUM INCLUDES ONLY ONE VECTOR FROM EACH SET OF P       048
C      IOU IS THE NUMBER OF VECTORS OF THE TYPE (B,C,D)                         049
   11  DO 400 J=1,JJJJ                                                         050
  400  READ(5,5)VK(J),B(J),C(J),D(J),IOU(J)                                    051
    5  FORMAT(1XE16.8      ,3F6.2,I5)                                           052
       IF(KKR.EQ.2)GOTO 402                                                     053
C      READ FOURIER COEFFICIENTS OF EXCHANGE                                    054
   17  DO401 J=1,JJJJ                                                          055
  401  READ(5,5)RK(J)      ,B(J),C(J),D(J),IOU(J)                               056
  402  CONTINUE                                                                 057
C      READ S WAVEFUNCTIONS FOR VANADIUM IN THE FOLLOWING ORDER                 058
C EXPONENT  1-S COEFF       2-S COEFF       3-S COEFF       4-S COEFF           059
C 22.77   0.20690816D 03 -0.643931167D 02  0.230745810 02 -0.508492980 01       060
C 36.05   0.915713640 01  0.822626920-01  0.181843850 00 -0.199162310 00       061
C 19.54   0.670688630 02 -0.307861870 03  0.127452280 03 -0.316925230 02       062
C 9.374   0.128922830 01  0.323291850 03 -0.130765020 03  0.309352650 02       063
C 7.905  -0.214329590 01  0.736450550 02 -0.148713120 03  0.316692470 02       064
C 5.130   0.711613370 CC -0.300630860 C1  0.944602290 02 -0.141819900 02       065
C 3.902  -0.281601090 00  0.137781620 01  0.772943010 01 -0.941408750 01       066
C 3.75    0.923483470-01 -0.417293710 00  0.172251250 02  0.130754900 00       067
C 1.658  -0.153342150-03  0.722898720-03  0.109858700-01  0.580071460 00       068
C 0.995   0.110044370-04 -0.506204090-04 -0.516108080-03  0.592930060-01       069
C 0.676  -0.776445400-06  0.368811560-05  0.347459310-04  0.532253320-03       070
```

```
      DO10 J=1,11                                                       071
      I=4*J-3                                                           072
      K=4*J-2                                                           073
      L=4*J-1                                                           074
      M=4*J                                                             075
   10 READ(5,3)ALD(J),CD(I),CD(K),CD(L),CD(M),IEX(J)                    076
    3 FORMAT(F8.5,4D16.8,I5)                                            077
C     READ DIRECT LATTICE COORDINATES                                   078
   60 READ(5,4)AX,AY,AZ,BX,BY,BZ,CX,CY,CZ                              079
    4 FORMAT(9F8.5)                                                     080
      DO398J=1,10                                                       081
      SOL1(J)=0.0                                                       082
      SS(J)=0.D0                                                        083
  398 SOLD(J)=0.D0                                                      084
C     SUM OVER ALL DIFFERENT PAIRS OF EXPONENTS                         085
      DO40L=1,11                                                        086
      DO 40 K=1,L                                                       087
      CDC(1)=CD(4*K-3)*CD(4*L-3)                                        088
      CDC(2)=CD(4*K-3)*CD(4*L-2)                                        089
      CDC(3)=CD(4*K-3)*CD(4*L-1)                                        090
      CDC(4)=CD(4*K-3)*CD(4*L)                                          091
      CDC(5)=CD(4*K-2)*CD(4*L-2)                                        092
      CDC(6)=CD(4*K-2)*CD(4*L-1)                                        093
      CDC(7)=CD(4*K-2)*CD(4*L)                                          094
      CDC(8)=CD(4*K-1)*CD(4*L-1)                                        095
      CDC(9)=CD(4*K-1)*CD(4*L)                                          096
      CDC(10)=CD(4*K)*CD(4*L)                                           097
      CDC(11)=CD(4*K-2)*CD(4*L-3)                                       098
      CDC(12)=CD(4*K-1)*CD(4*L-3)                                       099
      CDC(13)=CD(4*K)  *CD(4*L-3)                                       100
      CDC(14)=CD(4*K-1)*CD(4*L-2)                                       101
      CDC(15)=CD(4*K)  *CD(4*L-2)                                       102
      CDC(16)=CD(4*K)  *CD(4*L-1)                                       103
      IF(L.EQ.K)GOTO 50                                                 104
      CDC(1) =2.0*CDC(1)                                                105
      CDC(2) =CDC(2)+CDC(11)                                            106
```

```
      CDC(3) =CDC(3)+CDC(12)                                            107
      CDC(4) =CDC(4)+CDC(13)                                            108
      CDC(5) =2.0*CDC(5)                                                109
      CDC(6) =CDC(6)+CDC(14)                                            110
      CDC(7) =CDC(7)+CDC(15)                                            111
      CDC(8) =2.0*CDC(8)                                                112
      CDC(9) =CDC(9)+CDC(16)                                            113
      CDC(10)=2.0*CDC(10)                                               114
   50 ALPHA1=ALD(L)                                                     115
      ALPHA2=ALD(K)                                                     116
      IE=IEX(K)                                                         117
      IX=IEX(L)                                                         118
      CON35=ALPHA1*ALPHA1/3.0                                           119
      CON36=ALPHA2*ALPHA2/3.0                                           120
      CON38=ALPHA1*ALPHA1                                               121
      CON39=ALPHA2*ALPHA2                                               122
      CON40=CON38*CON39                                                 123
      CON41=CON40*ALPHA1                                                124
      CON42=CON38*ALPHA1                                                125
      CON43=CON39*ALPHA1                                                126
      CON44=CON40*ALPHA2                                                127
      CON45=CON42*ALPHA2                                                128
      CON46=CON39*ALPHA2                                                129
      CON47=CON46*ALPHA1                                                130
      CON48=ALPHA1*ALPHA2                                               131
      CON49=CON46/ALPHA1                                                132
      CON50=CON42/ALPHA2                                                133
      CON51=ALPHA1/ALPHA2                                               134
      CON52=ALPHA2/ALPHA1                                               135
      CON53=1.0/ALPHA1                                                  136
      CON54=1.0/ALPHA2                                                  137
      CON55=1.0/CON48                                                   138
      CON56=CON39*CON53                                                 139
      CON57=CON51*ALPHA1                                                140
      CON58=CON48*ALPHA1                                                141
      RAB=DSQRT((BX-AX)**2+(BY-AY)**2+(BZ-AZ)**2)                       142
```

```
      AA=C.5DO      *ALPHA1*ALPHA2*RAB**3                                    143
      DO100N=1,10                                                            144
      SUM1(N)=0.0                                                            145
  100 SUM(N)=0.DO                                                            146
C     SUM THE FOURIER SERIES                                                 147
      DO5CO J=1,JJJJ                                                         148
      DO8OKOL=1,100                                                          149
   80 FU(KOL)=0.DO                                                           150
      N=IOU(J)                                                               151
      AI=3.14159265/QA*B(J)                                                  152
      AJ=3.14159265/QA*C(J)                                                  153
      AK=3.14159265/QA*D(J)                                                  154
      SK=   DSQRT(AI*AI+AJ*AJ+AK*AK)                                         155
      RS=SK*SK                                                               156
C                                                                            157
C     SUBROUTINES D3INT,AGET,AND INTEG COMPUTE THE THREE-CENTER INTEGRAL     158
C     IF THE INTEGRALS HAVE BEEN STORED ON TAPE,READ THE TAPE INSTEAD OF     159
C     CALLING D3INT                                                          160
C                                                                            161
C     CALL D3INT                                                             162
C     SINT(KJ)=S(1)                                                          163
C     KJ=KJ+1                                                                164
C     IF(KJ.NE.3)GOTO 631                                                    165
C     WRITE(3)SINT(1),SINT(2)                                                166
C     KJ=1                                                                   167
      IF(KJ.EQ.2)GOTO 819                                                    168
C     READ INTEGRALS IN PAIRS FROM TAPE                                      169
      READ(3) SINT(1),SINT(2)                                                170
      KJ=1                                                                   171
  819 S(1)=SINT(KJ)                                                          172
      KJ=KJ+1                                                                173
  631 DO 777N=1,9                                                            174
  777 S(N+1)=S(1)                                                            175
      DO146N=1,10                                                            176
      IF(J.NE.1)GOTO145                                                      177
      SS(N)=SS(N)+S(N)*CDC(N)                                                178
```

```
  145 GOTO (147,148,148),KKR                                              179
      STOP                                                                180
  148 SUM1(N)=SUM1(N)+RK(J)*S(N)                                          181
      IF(KKR.EQ.2)GOTO 146                                                182
  147 SUM(N)=SUM(N)+VK(J)*S(N)                                            183
  146 CONTINUE                                                            184
  500 CONTINUE                                                            185
      DO40 J=1,10                                                         186
      SOL1(J)=SOL1(J)+SUM1(J)*CDC(J)                                      187
  408 SOLD(J)=SUM(J)*CDC(J)+SOLD(J)                                       188
   40 CONTINUE                                                            189
      WRITE(6,2)AX,AY,AZ                                                  190
      WRITE(6,2)BX,BY,BZ                                                  191
      WRITE(6,2)CX,CY,CZ                                                  192
    2 FORMAT(1X,3F10.6)                                                   193
C                                                                         194
C     COMPUTE KINETIC ENERGY INTEGRALS                                    195
C     SEE SUBROUTINE SZE FOR DESCRIPTION OF THE PARAMETERS                196
C                                                                         197
      LA=0                                                                198
      LB=0                                                                199
      MB=0                                                                200
      MA=0                                                                201
      CA=23.                                                              202
      CB=23.                                                              203
      CALL FACGEN(BF)                                                     204
      CALL AGENT(INDA,AFUN)                                               205
      OD=RAB                                                              206
      DO700 J=1,10                                                        207
  700 EK(J)=0.DO                                                          208
      DO200 J=1,11                                                        209
      DO200 K=1,J                                                         210
      XA=ALO(J)                                                           211
      XB=ALO(K)                                                           212
      IX=IEX(J)                                                           213
      IE=IEX(K)                                                           214
```

```
      NA=IX+1                                                          215
      NB=IE+1                                                          216
      COJ(1)=0.25D0/(XA*XB)**1.5                                       217
      COJ(2)=0.43301270/(XA**2.5*XB**1.5)                              218
      COJ(3)=1.18585412 /(XA**3.5*XB**1.5)                             219
      COJ(4)=4.43705983/(XA**4.5*XB**1.5)                              220
      COJ(5)=7.68521307/(XA**4.5*XB**2.5)                              221
      COJ(6) =21.04682276/(XA**4.5*XB**3.5)                            222
      COJ(7) =78.75D0/(XA*XB)**4.5                                     223
      COJ(8) =2.05395958/(XA**3.5*XB**2.5)                             224
      COJ(9) =5.625DC/(XA*XB)**3.5                                     225
      COJ(10)=0.75D0/(XA*XB)**2.5                                      226
      IF(IX.NE.0.OR.IE.NE.0) GOTO 2000                                 227
      ABK=2.DO                                                         228
      I=1                                                              229
      GOTO 749                                                         230
2000  IF(IX.NE.1.OR.IE.NE.0) GOTO 2001                                 231
      ABK=2.DC/DSQRT(3.DO)                                             232
      I=2                                                              233
      GOTO 749                                                         234
2001  IF(IX.NE.2.OR.IE.NE.0) GOTO 2002                                 235
      ABK=4.DO/(3.DO*DSQRT(10.DO))                                     236
      I=3                                                              237
      GOTO 749                                                         238
2002  IF(IX.NE.3.OR.IE.NE.C) GOTO 2003                                 239
      ABK=2.DC/(3.DO*DSQRT(35.DO))                                     240
      I=4                                                              241
      GOTO 749                                                         242
2003  IF(IX.NE.1.OR.IE.NE.1) GOTO 2005                                 243
      ABK=2.DO/3.DO                                                    244
      I=10                                                             245
      GOTO 749                                                         246
2005  IF(IX.NE.2.OR.IE.NE.1) GOTO 2006                                 247
      ABK=4.DO/(3.DO*DSQRT(30.DO))                                     248
      I=8                                                              249
      GOTO 749                                                         250
```

```
2006 IF(IX.NE.3.OR.IE.NE.1) GOTO 2007                                    251
     ABK=2.DO/(3.DO*DSQRT(105.DO))                                       252
     I=5                                                                 253
     GOTO 749                                                            254
2007 IF(IX.NE.2.OR.IE.NE.2)GOTO 2010                                     255
     ABK=4.DO/45.DO                                                      256
     I=9                                                                 257
     GOTO 749                                                            258
2010 IF(IX.NE.3.OR.IE.NE.2)GOTO 2011                                     259
     ABK=4.DO/(45.DO*DSQRT(14.DO))                                       260
     I=6                                                                 261
     GOTO 749                                                            262
2011 ABK=2.DO/315.DO                                                     263
     I=7                                                                 264
 749 CALL SZE(E,ZA,ZB,NA,LA,MA,XA,CA,NB,LB,MB,XB,CB,ABK,INDA,AFUN)       265
     E=E*COJ(I)*2.0                                                      266
     CDC(1)=CD(4*K-3)*CD(4*J-3)                                          267
     CDC(2)=CD(4*K-3)*CD(4*J-2)                                          268
     CDC(3)=CD(4*K-3)*CD(4*J-1)                                          269
     CDC(4)=CD(4*K-3)*CD(4*J)                                            270
     CDC(5)=CD(4*K-2)*CD(4*J-2)                                          271
     CDC(6)=CD(4*K-2)*CD(4*J-1)                                          272
     CDC(7)=CD(4*K-2)*CD(4*J)                                            273
     CDC(8)=CD(4*K-1)*CD(4*J-1)                                          274
     CDC(9)=CD(4*K-1)*CD(4*J)                                            275
     CDC(10)=CD(4*K)*CD(4*J)                                             276
     CDC(11)=CD(4*K-2)*CD(4*J-3)                                         277
     CDC(12)=CD(4*K-1)*CD(4*J-3)                                         278
     CDC(13)=CD(4*K)  *CD(4*J-3)                                         279
     CDC(14)=CD(4*K-1)*CD(4*J-2)                                         280
     CDC(15)=CD(4*K)  *CD(4*J-2)                                         281
     CDC(16)=CD(4*K)  *CD(4*J-1)                                         282
     IF(K.EQ.J)GOTO 710                                                  283
     CDC(1) =2.0*CDC(1)                                                  284
     CDC(2) =CDC(2)+CDC(11)                                              285
     CDC(3) =CDC(3)+CDC(12)                                              286
```

```
      CDC(4) =CDC(4)+CDC(13)                                                    287
      CDC(5) =2.0*CDC(5)                                                        288
      CDC(6) =CDC(6)+CDC(14)                                                    289
      CDC(7) =CDC(7)+CDC(15)                                                    290
      CDC(8) =2.0*CDC(8)                                                        291
      CDC(9) =CDC(9)+CDC(16)                                                    292
      CDC(10)=2.0*CDC(10)                                                       293
  710 DO701 L=1,10                                                              294
  701 EK(L)=EK(L)+E*CDC(L)                                                      295
  200 CONTINUE                                                                  296
      N1=AX/QA+0.1                                                              297
      N2=AY/QA+0.1                                                              298
      N3=AZ/QA+0.1                                                              299
      PUNCH 108,N1,N2,N3                                                        300
  108 FORMAT(3I5)                                                               301
      DO407J=1,10                                                               302
      IF(KKR.NE.3)GOTO 28                                                       303
      PUNCH 107,SOLD(J),EK(J),SOLI(J),SS(J)                                     304
  107 FORMAT(4E16.8)                                                            305
   28 KK=2 *J-1                                                                 306
      WRITE(6,8)GER(KK),GER(KK+1)                                               307
    8 FORMAT(1X,2A3)                                                            308
      WRITE(6,1)SOLD(J),EK(J),SOLI(J),SS(J)                                     309
    1 FORMAT(1X,'POTENTIAL=',E16.8,' KINETIC ENERGY=',F16.8,' EXCHANGE='        310
     1,E16.8,' OVERLAP=',E16.8)                                                 311
      WRITE(6,974)                                                              312
  974 FORMAT(1X,1H )                                                            313
  407 CONTINUE                                                                  314
      GO TO 60                                                                  315
      END                                                                       316
```

```
      SUBROUTINE AGET (EAX)                                              000
      IMPLICIT REAL*8(A-H,O-Z)                                           001
      DIMENSION S   (20)                                                 002
      DIMENSION FU(100) ,A(9),W(96),V(96)                                003
      COMMON/BIGS/CON35,CON36,CON38,CON39,CON40,CON41,CON42,CON43,        004
     1CON44,CON45                                                        005
     1,CON46,CON47,CON48,CON49,CON50,CON51,CON52,CON53,CON54,CON55,CON56  006
     2,CON57,CON58,S,W,V,U,A,RAB,ALPHA1,ALPHA2,RS,FU,AI,AJ,AK,AX,AY,AZ,  007
     3BX,BY,BZ,CX,CY,CZ,AA,N,IE,IX                                       008
      F=U*(1.-U)*RAB**2                                                  009
      G=RS+ALPHA2**2/(1.-U)+ALPHA1**2/U                                  010
      FG=F*G                                                             011
      DOB=DSQRT(FG)                                                      012
      D1=DOB**3                                                          013
      D2=DOB*D1                                                          014
      D3=D2*DOB                                                          015
      D4=D1*D1                                                           016
      D5=D1*D2                                                           017
      D6=D2*D2                                                           018
      D7=D1*D4                                                           019
      D8=D3*D3                                                           020
      D9=D1*D6                                                           021
      D10=D4*D4                                                          022
      D11=D4*D5                                                          023
      D12=D5*D5                                                          024
      D13=D5*D6                                                          025
      D14=D6*D6                                                          026
      C15=D6*D7                                                          027
      A(1)=F*(3./D3+3./D2+1./D1)                                         028
      A(2)=F*F*(15./D5+15./D4+6./D3+1./D2)                               029
      A(3)=F**3*(105./D7+105./D6+45./D5+10./D4+1./D3)                    030
      A(4)=F**4*(945./D9+945./D8+420./D7+105./D6+15./D5+1./D4)           031
      A(5)=F**5*(10395./D11+10395./D10+4725./D9+1260./D8+210./D7+21./D6  032
     1+1./D5)                                                            033
      A(6)=F**6*(135135./D13+135135./D12+62370./D11+17325./D10+3150./D9  034
```

```
     1+378./D8+28./D7+1./D6)                                                    035
      A(7)=F**7*(2027025./D15+2027025./D14+945945./D13+270270./D12+             036
     1 51975./D11+6930./D10+630./D9+36./D8+1./D7)                               037
      IF(D08.GT.90.)GOTO 222                                                    038
      EAX=DEXP(-D08)                                                            039
      GOTO 223                                                                  040
  222 EAX=0.0                                                                   041
  223 RETURN                                                                    042
      END                                                                       043
```

```
      SUBROUTINE INTEG                                                      000
      IMPLICIT REAL*8(A-H,C-Z)                                              001
      DIMENSION S  (20)                                                     002
      DIMENSION FU(100) ,A(9),W(96),V(96)                                   003
      COMMON/BIGS/CON35,CON36,CON38,CON39,CON40,CON41,CON42,CON43,           004
     1CON44,CON45                                                           005
     1,CON46,CON47,CON48,CON49,CON50,CON51,CON52,CON53,CON54,CON55,CON56     006
     2,CON57,CON58,S,W,V,U,A,RAB,ALPHA1,ALPHA2,RS,FU,AI,AJ,AK,AX,AY,AZ,     007
     3BX,BY,BZ,CX,CY,CZ,AA,N,IE,IX                                          008
      DO 50 J=1,96                                                          009
50    S(1)=S(1)+W(J)*FU(J)                                                  010
      S(1)=S(1)*0.500                                                       011
      RETURN                                                                012
      END                                                                   013
```

```
      SUBROUTINE D3INT                                                      000
      IMPLICIT REAL*8(A-H,C-Z)                                              001
      DIMENSION S  (20)                                                     002
      DIMENSION FU(100) ,A(9),W(96),V(96)                                   003
      COMMON/BIGS/CON35,CON36,CON38,CON39,CON40,CON41,CON42,CON43,           004
     1CON44,CON45                                                           005
     1,CON46,CON47,CON48,CON49,CON50,CON51,CON52,CON53,CON54,CON55,CON56     006
     2,CON57,CON58,S,W,V,U,A,RAB,ALPHA1,ALPHA2,RS,FU,AI,AJ,AK,AX,AY,AZ,     007
     3BX,BY,BZ,CX,CY,CZ,AA,N,IE,IX                                          008
      S(1)=0.D0                                                             009
      TOM1=CON42*CON46                                                      010
      TOM2=CON46*ALPHA1                                                     011
      CON=N                                                                 012
206   DO 750 J=1,96                                                         013
      U=(V(J)+1.D0)*0.5D0                                                   014
      DX=AX*U+BX*(1.-U)                                                     015
      DY=AY*U+BY*(1.-U)                                                     016
      DZ=AZ*U+BZ*(1.-U)                                                     017
      RCDX=DX-CX                                                            018
      RCDY=DY-CY                                                            019
      RCDZ=DZ-CZ                                                            020
      C1=DCOS(AI*RCDX)                                                      021
      C2=DCOS(AJ*RCDY)                                                      022
      C3=DCOS(AK*RCDZ)                                                      023
      CO=C1*C2*C3*CON                                                       024
      CAB=1.0-U                                                             025
      HH=U*(1.0-U)                                                          026
      HHH=HH*HH                                                             027
      HHHH=HHH*HH                                                           028
      CAB2=U*U                                                              029
      CAB3=CAB*CAB                                                          030
      CAB4=U*HH                                                             031
      CAB5=CAB*HH                                                           032
      CAB6=HHH*U                                                            033
      CAB7=CAB2*HH                                                          034
```

```
      CAB8=CAB3*HH                                                          035
      CAB9=CAB2*U                                                           036
      CAB10=CAB3*CAB                                                        037
      CALL AGET(EAX)                                                        038
      IF(EAX.EQ.0.0)GOTO750                                                 039
C                                                                           040
C     FOLLOWING ARE THE 10 DIFFERENT S-S INTEGRAL FORMULAS FOR 1S THROUG    041
C                                                                           042
      IF(IX.NE.0.OR.IE.NE.0) GOTO 2000                                      043
      FU(J)=A(1)*CO*EAX*AA                                                  044
      GOTO 750                                                              045
 2000 IF(IX.NE.1.OR.IE.NE.0) GOTO 2001                                      046
      FU(J)=(-CON53*A(1)+ALPHA1/U*A(2))*CO*EAX*AA                           047
      GOTO 750                                                              048
 2001 IF(IX.NE.2.OR.IE.NE.0) GOTO 2002                                      049
      FU(J)=(-3./U*A(2)+CON38/CAB2*A(3))*CO*EAX*AA                          050
      GOTO 750                                                              051
 2002 IF(IX.NE.3.OR.IE.NE.0) GOTO 2003                                      052
      FU(J)=(3.*CON53/U*A(2)-6.*ALPHA1/CAB2*A(3)+CON42*A(4)/CAB9)           053
     1*EAX*CO*AA                                                            054
      GOTO 750                                                              055
 2003 IF(IX.NE.1.OR.IE.NE.1) GOTO 2004                                      056
      FU(J)=(A(1)-(CON39/CAB+CON38/U)*A(2)+CON40/HH*A(3))*EAX*CO*CON55      057
     1*AA                                                                   058
      GOTO 750                                                              059
 2004 IF(IX.NE.2.OR.IE.NE.1) GOTO 2005                                      060
      FU(J)=(3./U*A(2)-(CON38/CAB2+3.*CON39/HH)*A(3)+CON40/CAB4*A(4))*      061
     1CON54*CO*EAX*AA                                                       062
      GOTO 750                                                              063
 2005 IF(IX.NE.3.OR.IE.NE.1) GOTO 2006                                      064
      FU(J)=(-3.*CON55*A(2)/U +(6.*CON51/CAB2+3.*CON52/HH)*A(3)-(CON50/     065
     1CAB9+6.*CON48/CAB4)*A(4)+CON45/CAB7*A(5))*CO*EAX*AA                   066
      GOTO 750                                                              067
 2006 IF(IX.NE.2.OR.IE.NE.2)GOTO 2007                                       068
      FU(J)=(9./HH*A(3)+CON40/HHH*A(5)-3.*(CON38/CAB4+CON39/CAB5)*A(4))     069
     1*EAX*CO*AA                                                            070
```

```
      GOTO 750                                                          071
 2007 IF(IX.NE.3.OR.IE.NE.2)GOTO 2008                                   072
      FU(J)=(CON41*A(6)/CAB6-(6.*CON43/HHH+3.*CON42/CAB7)*A(5)+(18.*     073
     1ALPHA1/CAB4+3.*CON39*CON53/CAB5)*A(4)-9.*CON53/HH*A(3))*CO*EAX*AA  074
      GOTO 750                                                          075
 2008 FU(J)=(TOM1 /HHHH*A(7)-6.*(CON45/CAB6+TOM2 /(HHH*CAB))*A(6)+(36.  076
     1*CON48/HHH+3.*CON49/CAB8+3.*CON50/CAB7)*A(5)-18.*(CON51/CAB4+CON52 077
     2/CAB5)*A(4)+9.*A(3)/(HH*CON48))*CO*EAX*AA                         078
  750 CONTINUE                                                          079
      CALL INTEG                                                        080
      RETURN                                                            081
      END                                                               082
C                                                                       083
C                                                                       084
C     AT THIS POINT INSERT THE KINETIC ENERGY GROUP OF SUBROUTINES AS    085
C     LISTED EARLIER.  THESE ARE SZE, FACGEN, AGENT, PORN, AND DOUBLE   086
C     PRECISION FUNCTION.                                               087
C                                                                       088
C                                                                       089
```

VITA

Thomas E. Norwood was born on January 9, 1943 in Montogomery, Alabama. He graduated from Robert E. Lee High School, Montgomery, Alabama, in 1961. He received the degree of Bachelor of Arts in Physics from Vanderbilt University, Nashville, Tennessee in 1965. He is now a candidate for the degree of Doctor of Philosophy in the Department of Physics and Astronomy.

EXAMINATION AND THESIS REPORT

Candidate: Thomas Ellis Norwood, III

Major Field: Physics

Title of Thesis: Energy Bands of Vanadium Oxide

Approved:

John L. Fry
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Wilbraun Lamp

R D Anderson

R. W. LaBahn

Joseph Callaway

Date of Examination:

7 October 1969